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RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY

INTRODUCTORY

With the opening number of RUBBER CHEMISTRY AND TECHNOLOGY it may not be amiss to offer a few words about the growth of an idea which has culminated in this latest undertaking of the Rubber Division of the American Chemical Society.

In recent years the majority of papers presented at the semi-annual meetings of the Rubber Division have been published in *Industrial & Engineering Chemistry*, a few have appeared in the trade journals, occasionally one has been published in the *Journal of the American Chemical Society*, while still others have never been published at all. In general, papers on rubber chemistry which have been published in the United States are scattered among widely different journals. To these must be added the numerous excellent papers in foreign journals, and in the latter case the number of journals containing frequent or occasional important articles is greater still. This is well illustrated by the recent appearance of a long paper on accelerators* in the *Memoirs of the College of Engineering at Kyushi Imperial University*, Japan.

The average rubber chemist is unfortunate in having available only a few journals, most of which, though devoted to rubber, contain relatively few contributions of permanent value. He has been obliged to rely upon *Chemical Abstracts* or other abstract journals for many important papers, and often the abstract has remained his only acquaintance with the work. A few trade journals have now and then translated important articles, but the rubber chemist never knows whether an important work published in a rare or inaccessible journal will appear in full or whether he will have to be content with an abstract.

It is therefore not surprising that it has come to be realized that there is opportunity for improvement in the publication of papers on the chemistry and technology of rubber. At the Richmond meeeting of April, 1927, there was for the first time a discussion of the advisability of publishing papers on rubber chemistry and technology in separate convenient form. Later a general vote showed a large majority in favor of such a venture, and at the Detroit meeting of September, 1927, the Rubber Division formally voted to begin a new publication which would contain reprints of all papers presented before the Division and accepted for publication by the Society journals or released to other journals.

The new journal was to be financed by the dues of the members of the Rubber Division, by subscriptions of non-members and by corporate subscriptions of rubber companies, companies supplying the rubber industry, other companies and of municipal or institution libraries. Because of its sponsorship by the Rubber Division it was further decided that it should be edited by a board chosen from the members of the Division.

With this as a background, the task has been undertaken to fulfill the commands of the Rubber Division and to publish an opening number of RUBBER CHEMISTRY AND TECHNOLOGY. It has been impossible to publish all recent papers of permanent value which have appeared elsewhere than in the Society journals, but a beginning has been made, and this first number contains records of recent and future activities of the Rubber Division, gives a bird's-eye view in the form of abstracts of recent literature, presents all papers of the Detroit Meeting, contains five papers chosen from German, Italian and British journals, and finally gives the recent Report of the Physical Testing Committee. It also inaugurates an attempt to aid the busy chemist in avoiding the inconvenience of foreign languages.

* This paper will be published in the second issue of RUBBER CHEMISTRY AND TECHNOLOGY.

The importance of articles translated into English must not be underestimated, for the chemist often fails to study a paper because it is in a language which requires an effort on his part to read, and then again some important papers appear in languages with which most chemists are unfamiliar. As the scope and importance of RUBBER CHEMISTRY AND TECHNOLOGY increase, it will be possible to publish more translated papers from foreign publications and thus to fulfill a long-felt desire expressed by many that papers in German, French, or Italian may be available in English. This feature in itself should make everyone wish for the success of the journal and contribute toward placing it on a secure financial basis so that it may become a comprehensive journal and a general medium for the publication in English of all papers dealing with the chemistry and technology of rubber.

Even in its present form, the new journal should be of value not only to the busy industrial chemist and technologist, but also to libraries, where compilations of important information under one cover are especially esteemed. As its convenience and utility are recognized, it is hoped that it will be so generously supported that it will bring periodically to the desk of the rubber chemist a compilation of all important literature on rubber, wherever published. When this comes about, the literature will no longer be scattered through a motley array of academic, industrial, engineering, and trade journals.

The Rubber Association of America, with keen foresight, was quick to realize the sound economy to the rubber industry of the new publication, and it has responded most generously; in fact, the present issue has been made possible in large measure by financial assistance of the Rubber Association.

The Rubber Division of the American Chemical Society is deeply indebted to the Association for this generous support through its President, Mr. Litchfield, its Secretary, Mr. Viles, and its Board of Directors, and the Association may be assured that its generosity will be reflected in a greater proficiency of the technical staffs of the rubber industry, with mutual advantage to all.

THE EDITOR

Announcements and Records

H. E. SIMMONS, Secretary-Treasurer of the Rubber Division of the American Chemical Society

The Rubber Division of the American Chemical Society

Officers

Chairman.....................HARRY L. FISHER, United States Rubber Co.
Vice Chairman..................ARNOLD H. SMITH, Rubber Service Laboratories
Secretary-Treasurer.............H. E. SIMMONS, Municipal University of Akron
Executive Committee..H. A. WINKELMANN, E. R. BRIDGWATER, STANLEY KRALL,
   J. M. FRYE, W. G. NELSON.

Coming Meetings

The Spring Meeting of the American Chemical Society will be held in St. Louis, April 16–19, 1928. The Headquarters of the Rubber Division are the Coronado Hotel.

The Fall Meeting of the American Chemical Society will be held September 10–13, 1928, at Swampscott, Mass.

Minutes of Recent Meetings

Minutes of the Detroit Meeting, Sept. 7–9, 1927

On Wednesday, Sept. 7, Papers 1 to 8 on the program as printed were presented and the Nominating Committee of Messrs. Spear, Boggs, and Simmons was appointed.

The attendance at the meeting on Sept. 7 varied from 200 to 250, on Sept. 8 from 185 to 225, and on Sept. 9 was about 170.

On Sept. 8 the Division took up the discussion of the new proposals as outlined in the circular letter to the Rubber Division concerning the extension of the activities of the division to provide for local sections and a unit publication.

Dr. H. E. Howe, Editor of *Industrial & Engineering Chemistry*, outlined the work that could be carried out by that journal.

Dr. Fisher moved to establish the reprint system as outlined, viz., that *Industrial & Engineering Chemistry* should reprint journal articles and other rubber articles published by the trade journals. The abstracts pertaining to rubber now appearing in *Chemical Abstracts* should be included in the reprint collections. Further details were to be arranged by the Executive Committee. The motion was seconded and passed.

Mr. Johnson moved that local groups of the Rubber Division be formed as required and that the Executive Committee be authorized to proceed with the formation of such groups when and where they deemed desirable. The motion was seconded and passed.

Balloting resulted in the election of the officers named at the beginning of this section.

The minutes of the previous meeting and the Secretary's financial report were read and accepted.

Mr. Partenheimer presented the report of the Physical Testing Committee. The motion was made, seconded, and passed for the acceptance of this report.

A summary report is to be published in the trade journals as promptly as possible. The complete report in detail is to be mimeographed and distributed to the members or to be included in the reprint journal. The question of financing the work of the Physical Testing Committee was still left in the hands of the Executive Committee. It was understood that Mr. Dinsmore would complete the efforts he had started to take care of this matter. Mr. Dinsmore will work with Dr. Fisher to complete the final arrangements.

The program was completed as printed.

A. H. SMITH, *Secretary-Treasurer*

Minutes of the Executive Committee of the Rubber Division

A meeting of the Executive Committee of the Rubber Division of the American Chemical Society was held in Akron, November 14, 1927, at which the following members were present: H. L. Fisher, A. H. Smith, W. G. Nelson, Stanley Krall, E. R. Bridgwater, H. A. Winkelmann, H. E. Simmons.

C. C. Davis was elected Editor of the reprints, with power to choose his associates.

W. W. Evans was elected Managing Editor with authority to select his own associates.

After some discussion of the financial situation in regard to the reprints, it was decided that the dues of the Division be raised to $2.00 per year and that of Associate Members to $4.00, provided that the financial situation required this; if not, the difference between dues of the members and the Associate Members would be $2.00.

It was also decided to suggest to the Managing Editor that we would try and secure subscriptions to the reprints from the industry at $10.00 per year and that the same efforts be made with reference to public libraries.

After some discussion of the group meetings it was decided that we would allow each group to work out its own program and method of procedure, and that we would ask A. A. Somerville to be in charge of the New York group, C. R. Boggs of the Boston group, R. P. Dinsmore of the Akron group, and R. B. Stringfield of the Los Angeles group.

The question of the Boston Meeting in regard to the polymerization symposium was discussed briefly. It was voted to have the headquarters of the Rubber Division at the Preston Hotel and for the meetings to be at the same hotel.

It was decided that the St. Louis Meeting would be composed of papers by individual members.

It was moved, seconded, and passed that the Chairman appoint two or three men to act as reviewers for each paper presented to the Division and to lead in the discussion of the paper, and that the reviewers give the Secretary the number of minutes that they should be allotted on the program for the respective papers.

It was moved and seconded that the titles of the papers be in the hands of the Secretary three months prior to the meeting and that the papers themselves must be in the hands of the Secretary six weeks prior to the meeting. This would enable the papers to appear in the first issue of *Industrial & Engineering Chemistry* immediately following the meeting. This motion was amended to read, "that this procedure should go into effect with the Boston Meeting." This motion was passed.

It was moved, seconded, and passed that the titles and papers for the Spring Meeting must be in the hands of the Secretary six weeks prior to the meeting.

F. W. Frerichs of Cupples Co., 600 Spruce St., St. Louis, Mo., was appointed chairman of the arrangements for the Rubber Division at the St. Louis Meeting to include chairmanship of the banquet.

The Executive Committee adjourned for lunch at the University Club where it

was joined by R. P. Dinsmore of the Goodyear Tire and Rubber Company. Following the lunch Mr. Dinsmore gave us a report in regard to the financial situation of the work of the Committee on Physical Testing. At this meeting he stated that Mr. Litchfield would recommend to the Rubber Association of America a continuation of funds for carrying on the physical testing for another year.

After a general discussion the Committee adjourned.

H. E. Simmons, *Secretary*

Meetings of Local Groups

On January 11, 1928, the first meeting of the New York Group was addressed by Mr. F. R. Henderson, President of the Rubber Exchange, New York, whose subject was "The Buying and Selling of Crude Rubber." At this meeting W. A. Gibbons of the United States Rubber Company was chosen Chairman and D. F. Cranor of Binney and Smith Co., Secretary-Treasurer.

On January 20 the Los Angeles Group was addressed by Herbert A. Endres, research chemist of the Celite Company of Lompoc, Calif. His subject was "Crystallization of Sulfur in Rubber and the Phenomenon of Blooming."

On February 15 the Akron Group held its meeting at the Akron City Club. The speaker was Dr. G. F. Lamb, Professor of Geology of Mt. Union College, whose address was "The Distribution and Seasonal Fluctuation of Akron's Water Supply Both Surface and Underground."

Financial Statement

Received October 15 from former Secretary-Treasurer A. H. Smith	$298.86	
Disbursements from Oct. 15 to Feb. 22 .... $42.37		
Amount deposited (dues)	171.00	$469.86
Expenditures		42.37
Balance on hand Feb. 22, 1928		$427.49

H. E. Simmons, *Secretary-Treasurer*

A Survey of Recent Literature on the Chemistry of Rubber

Abstracts of Articles Pertaining to the Chemistry of Rubber Which Have Appeared in Foreign and American Journals

The following abstracts are reprinted from the February 10 and 20, and March 10 and 20, 1928, issues of *Chemical Abstracts* and, with earlier and succeeding issues, they form a complete record of all chemical work published in the various academic, engineering, industrial and trade journals throughout the world.

Latex as a marketable grade of rubber. H. N. BLOMMENDAAL AND N. H. VAN HARDEN. *Arch. Rubbercultuur* **11**, 537–46(1927). (In English 547–55.)—A review of present developments in the *concn. and applications of latex.* Certain of the patents are described in detail. C. C. DAVIS

Variability of Ceylon estate grades of rubber. LONDON COMMITTEE CEYLON RUBBER RESEARCH SCHEME. *Bull. Imp. Inst.* **25**, 218–42; *India Rubber J.* **74**, 861–3, 899(1927).—The variability of smoked sheets, air-dried crepe and machine-dried crepe was studied by testing the plasticity, time of cure and tensile strength of rubber-S mixts., and the phys. properties of rubber-S-diphenylguanidine-ZnO mixts. of representative samples from 24 estates. The plasticity of air-dried and machine-dried crepes varied considerably, but not so much as that of smoked sheet, the limiting values for air-dried crepe, machine-dried crepe and smoked sheets being 0.9–18.7, 11.7–26.4 and 8.8–26.8, resp. The large variation in machine-dried crepe depended upon a few exceptional samples and in general this crepe was not only more plastic but was much more uniform than air-dried crepe and smoked sheets. The plasticity values indicate that the temp. of drying is of importance in governing plasticity and that smoking is of aid in rendering rubber more readily plasticized. The av. times of cure of rubber-S mixts. were 118, 128 and 125 min. for smoked sheets, air-dried crepe and machine-dried crepe, resp., with variations of −8 to +16%, −13 to +17% and −6 to +11%, resp. The tensile strengths of the cured rubber-S mixts. varied in all 3 cases about 10% above and below the av. values. It is considered that this variation is not serious. Off-grade rubber has, however, a much lower tensile strength, which may be only 0.5 that of high-grade rubber, so this test is of special value as a criterion of quality. In accelerated mixts., the ultimate elongation varied only from 559 to 609%, while the tensile strength varied from 2690 to 3300 lb. per sq. in., variations which are considered of no importance. No relation could be found between plasticity and any of the other tests except rate of vulcanization. In general soft rubbers had a slow rate of vulcanization and tough rubbers a rapid one, a property which may be explained by the fact that the tough rubbers may have undergone *maturation.* The results indicate the importance of detg. the reason why smoked sheets vary in plasticity, the effect of hot-air drying on plasticity and uniformity, the effect of the time of maturing the coagulum on plasticity, the uniformity of plasticity and phys. properties practicable under the most rigidly standardized conditions, and the effect of different proportions of compounding ingredients on uniformity. C. C. DAVIS

Synthetic rubbers. L. SLOÏM. *Rev. gén. caoutchouc* 1927, No. 35, 8–10; No. 36, 4–6; cf. *C. A.* **21**, 2815.—The problem of the constitution of rubber is reviewed, with special reference to the researches of Harries. C. C. DAVIS

The problem of the synthesis of rubber. A. MAXIMOFF. *Caoutchouc & gutta-percha* **24**, 13723–5(1927).—In view of the *structure of rubber* which has been proposed by M. (cf. *C. A.* **21**, 2819), the synthesis of rubber must include not only the chem. synthesis of at least 2 compds. but also the creation of a polyphase colloid system in the correct quant. proportions and with the structure and the properties already described. Though in past attempts at the synthesis of rubber, the formation of erythrene has been considered to be an undesirable secondary reaction, it is probable that because of its properties its formation or the formation of compds. of similar properties is essential to the ultimate synthesis of a polyphase elastic rubber. In general the synthesis

of rubber is one example of the synthesis of elastic substances by the creation of poly-phase colloid systems composed of liquid and solid phases in which the solid phase is the continuous phase and has a high resistance to rupture. The chem. compn. of such systems is secondary, and may include a wide range of compds.　　　C. C. DAVIS

Rubber-seed oil and its use in industry. RUDOLF DITMAR. *Caoutchouc & gutta-percha* **24**, 13725–8(1927).—Data are given on the viscosity of rubber-seed oil, using the viscometer of D. already described (*C. A.* **20**, 3096). It is a little less viscous than rapeseed oil. More S_2Cl_2 and more S are required to prep. white and brown *factices from rubber-seed oil* than the quantities required for other oils ordinarily used for the purpose. The products are inclined to be tacky and are good plasticizing agents for rubber mixts. contg. low proportions of rubber and high proportions of pigments and fillers or of reclaimed rubber. A review of earlier publications precedes the exptl. work.
　　　C. C. DAVIS

Chemistry and technology in the rubber industry. RICHARD WEIL. *Gummi-Ztg.* **42**, 412–4(1927).—An address.　　　C. C. DAVIS

Rubber solvents. D. F. TWISS. *India Rubber J.* **74**, 573–5, 739–41, 773–6(1927).— See *C. A.* **21**, 1904.　　　C. C. DAVIS

Influence of the sulfur-rubber ratio on the physical properties of hard rubber. D. E. PEARSALL. *India Rubber World* **77**, 70–2(1927).—The impact strength, trans-verse strength and tensile strength at room temp., the deformation when heated and the softening point were chosen as criteria for detg. the influence of the proportion of S to rubber in mixts. contg. smoked sheet 15, reclaimed rubber 30, S 9.4–17, hard rubber dust 32.75, C black 2, MgO 0.25, pine tar 4. In studying the phys. quality as a func-tion of the ratio of S to total rubber hydrocarbon content, the ratio of combined S to rubber was disregarded on account of the samples being vulcanized to a point where the free S was very low. With S/rubber ratios below 0.30, the phys. strength was poor and the flexibility and flow under stress or when heated were too great. With a ratio of 0.45 the phys. strength was practically a max. and the deflection a min. The mixts. with ratios from 0.30 to 0.45 were the most desirable for general use. Phys. tests are a better criterion than chem. tests for judging the utility of hard rubber and they should form the basis of specifications. The relative merits of the individual phys. tests and the best technic for their application are discussed.　　　C. C. DAVIS

Contribution of the colloid chemistry of rubber latex. II. Measurements of the surface tension of the latex of Hevea brasiliensis. E. A. HAUSER AND P. SCHOLZ. *Kautschuk* **1927**, 332–3; cf. *Kautschuk* **1927**, 304.—Ordinary methods are inapplicable and resort was had to the torsion method used by Lenard, von Dallwitz-Wagener and Zachmann (*C. A.* **18**, 2827) for measuring surface tensions. When fresh latex is dild. to $^1/_{64}$ its normal rubber content, *i. e.*, to about 0.55% rubber the surface tension de-creases to a min. ($\delta = 30.5$). With further diln. the surface tension increases pro-gressively, approaching that of water. Before diln. (35% rubber) the value of δ was 40.5, while that of water at 28–30° was 71–72, and at 18° was 73.5–75. For comparison the *surface tensions of coconut-oil soap, K oleate and soft soap solns.* of the same dilns. were made for comparison. With these soaps, the min. surface tension (22.5, 27.5 and 27, resp.) was reached at 0.14% concn. K oleate in particular had a great effect on the surface tension, a 0.00013% soln. showing a δ value of only 50. The precision of the results is about ± 1–2%. The addn. of 1.15% NH_3 as a preservative lowered the sur-face tension of undild. latex to a δ value of 35.5, probably because of formation of active proteins or amino compds. On keeping, the free alkali diminished greatly, probably as a result of the formation of $MgNH_4PO_4$.　　　C. C. D.

Rubber mixtures. W. B. WIEGAND. *Kautschuk* **1927**, 334–7(1927).—A review and discussion of the present status of *C black* in the rubber industry.　　　C. C. D.

New rules for the formulation of rubber mixtures. WERNER ESCH. *Kautschuk* **1927**, 337–45.—Methods of compounding rubber mixts. with the most recent cura-tives, antioxidants and other essential ingredients are described, with the inclusion of representative formulas for various uses.　　　C. C. DAVIS

Some remarks on antioxidants and rubber. (Reply to Ch. Moureu and Ch. Dufraisse.) GUSTAVE BERNSTEIN. *Rev. gén. caoutchouc* **1927**, No. 35, 3; cf. *C. A.* **21**, 4096.—A work by Gottlob (*La technologie du caoutchouc manufacturé* **1915**, 52) is cited to show that Fickendey specifically describes the inhibitory action of such substances as tannin.　　　C. C. DAVIS

Some remarks on antioxidants and rubber. CHARLES MOUREU AND CHARLES DUFRAISSE. *Rev. gén. caoutchouc* **1927**, No. 36, 3.—Reply (cf. preceding abstr.).
　　　C. C. DAVIS

Rubber and its future. J. DUGUÉ. *Rev. gén. caoutchouc* **1927**, No. 35, 11–4; cf. *C. A.* **21**, 4092.—Some of the most recent technical developments and probable future developments are discussed.　　　C. C. DAVIS

Rubber in relation to engineering. T. R. DAWSON. *Rubber Age* (London) **8,** 404–7(1927).—Present and possible uses are discussed. C. C. DAVIS

The testing of rubber goods at the Bureau of Standards. ANON. *Rubber Age* (N. Y.) **22,** 299–300(1927). C. C. DAVIS

Importance of temperature and humidity control in rubber testing. J. E. PARTEN-HEIMER. *Rubber Age* (N. Y.) **22,** 245–8(1927).—A report of progress by the Phys. Testing Committee of the Rubber Division, Am. Chem. Soc. It comprises an exptl. study of the influence of the temp. and relative humidity of the air on the stress-strain curves of rubber mixts. before curing and during the interim between curing and testing. Five representative rubber mixts. of different types were tested after exposure to different conditions of temp., relative humidity and for different lengths of time both before and after they had been cured to different states. The investigation proves that normal daily variations of temp. may influence the phys. tests as much as does a 25–40% change in the time of vulcanization. With change in the relative humidity, on the other hand, the phys. tests change comparatively little. Variations in the abs. humidity before curing may influence the tensile strength and modulus as much as do variations in the temp. after curing. In general lab. tests conducted without control of temp. or of humidity may give very erroneous and misleading results. It is recommended that, both before and after curing, rubber mixts. be maintained for 24–28 hrs. at 82° $\pm$ 2° F. and at 45% $\pm$ 3% relative humidity and the air during testing be maintained at 82° $\pm$ 2° F. If a temp. of 82° prior to curing is impracticable, it is recommended that the relative humidity at the prevailing temp. be such that the abs. humidity is the same as that recommended for the 82° F. basis. The proper humidity may be obtained by the use of a conditioning cabinet humified with a suitable satd. salt soln. H_2SO_4 soln. is less desirable for this purpose. C. C. DAVIS

Vulcanization and devulcanization of rubber. PAUL BARY. *Rev. gén. caoutchouc* 1927, No. 35, 5–7; No. 36, 3–4; cf. *C. A.* **21,** 4097.—The probable chemistry of vulcanization by S, the reversibility of the reaction, devulcanization and vulcanization in soln. are discussed. C. C. DAVIS

Micrographic studies of vulcanized rubber showing the evolution of the free sulfur. REGNAUD. *Chimie et industrie* **18,** 397–400(1927).—Photomicrographs have shown that in hot-vulcanized rubber the free S tends to work its way out to the surface, the process comprising successively *flocculation, coalescence* and *crystn. of the S.* The rate of evolution varies considerably in objects of the same nature subjected to the same vulcanizing treatment and used under the same conditions. The facts observed are regarded as a confirmation of the *colloidal theory of vulcanization.* The equil. established at the vulcanizing temp. between the rubber-S compd. and the uncombined S is disturbed on cooling to atm. temp., at which the S forms a supersatd. soln. in the rubber; but liberation of the S is hindered by the heterogeneous colloidal state of the medium. Vulcanized rubber can therefore be considered as a complex in continuous evolution towards a state of equil. which it can never attain. A. PAPINEAU-COUTURE

Modern electrified rubber mill. ANON. *Elec. World* **90,** 1081–4(1927).—A detailed illustrated account of the elec. equipment of the Kenmore plant of the Miller Rubber Co. A recent development is the application of low-speed synchronous motors. C. G. F.

Safety code for rubber mills and calenders. J. E. CONGDON. U. S. Bur. Labor Statistics, *Bull.* **447,** 11 pp.(1927). C. M. SALLS

New röntgenographic investigations of rubber and related substances. E. A. HAUSER. *Kautschuk* 1927, 228–30.—Beautiful new x-ray diffraction photographs are reproduced from (1) frozen rubber, unstretched, showing distinct Debye-Scherrer rings; (2) frozen rubber stretched, showing interference maxima characteristic of a fiber structure lying on the original rings; (3) smoked sheet stretched 500% very slowly, showing practically no pattern except the amorphous ring; (4) the same smoked sheet very rapidly extended 500%, showing an intense fiber pattern; (5) racked rubber, showing extremely sharp interference maxima, of which several appear for the first time in the absence of all traces of the amorphous ring; (6) stretched balata and (7) stretched guttapercha. The latter two show great similarity, though different from rubber, the identity period in the direction of the fiber axis being 9.4 A. U., compared with 7.68 for rubber. The no. of mols. of the elementary hydrocarbon is evidently between 2 and 8. New photographs of the insol. and sol. fractions of rubber prepd. by Feuchter and by Pummerer show that both gel-rubber and sol-rubber as well as the whole material show, in the drawn condition, normal interference patterns. It was necessary to maintain the sol-rubber in an atm. of CO_2. G. L. CLARK

X-rays applied to the study of rubber and similar materials. E. A. HAUSER, M. HÜNEMÖRDER AND P. ROSBAUD. *Rev. gén. caoutchouc* No. **34,** 5–9(1927).—The same as the preceding abstr. G. L. CLARK

Rubber pigments from the point of view of the manufacturer. C. A. KLEIN. *Trans. Inst. Rubber Industry* **3**, 248–62(1927).—A discussion of the close relation between the properties of pigments required by the *paint* and by the *rubber* industries.
C. C. DAVIS

Coagulation phenomena in Hevea latex. V. Alcohol, alum and sodium chloride. O. DE VRIES AND N. BEUMÉE-NIEUWLAND. *Arch. Rubbercultuur* **11**, 497–517(1927). (In English 518–26); cf. *C. A.* **21**, 2077.—In view of latex being a lyophilic colloid of low solvation, the influence of EtOH as a dehydrating agent and of alum and NaCl as typical discharging agents was investigated. The influence of these coagulants on heated latex was also studied. It is already known that the addn. of 0.5 vol. of 96% EtOH causes latex to coagulate immediately and 0.25 vol. to coagulate within a few hrs. Expts. show that with dild. latex a disproportionately large quantity of EtOH is necessary, *e. g.*, latex dild. 1:1 requires 1 vol. of EtOH and with latex dild. 1:9 coagulation cannot be effected. The presence of salts promotes coagulation, so that relatively less EtOH is necessary. It is improbable that coagulation by EtOH depends upon soln. by the EtOH of protective resinous colloids. Neither does the EtOH ppt. the proteins, for the N content of rubber coagulated by EtOH is not abnormally high. EtOH coagulates immediately the stiff paste obtained by adding 5% of NaOH to latex, and it also coagulates latex freed of N compds. by addn. of NaOH and dialysis, so that proteins do not play an important part in coagulation by EtOH. No adequate proof that coagulation by EtOH is wholly or partially dehydration could be obtained, but it is probable that EtOH destroys the stability of the "hydration" equil. Tests of the relative coalescing effect of alum and of NaCl (cf. de V., *Estate Rubber* **181**, 189; *C. A.* **14**, 3168) showed that when based on equal wts. the coagulation effect of the Al ions is notably greater than that of the Na ion, and based on mg.-mols. per l. this difference is still greater. In very dil. latex, in which the additional effect of other serum substances is negligible, Al salts are still good coagulants, whereas NaCl has no coagulating power. In expts. on the relative effects of EtOH, alum and NaCl on fresh and on heated latex at different dilns., only the lower limit of the 1st zone of coagulation being considered, it was found that the limit in heated latex is at a lower concn., particularly with NaCl, than in fresh latex, with a tendency toward more rapid flocculation at first in the heated latex. There is, however, no reason to assume that the degree of hydration in heated latex is essentially different from that in fresh latex or the former is lyophobic and the latter lyophilic. In both the rubber is lyophilic, with a low degree of hydration. The slightly greater tendency for heated latex to coagulate is probably a result of changes in some of the non-rubber components. NaCl has no coalescing power, and even when B mixt. is satd. with NaCl, the flocculent mass remains unchanged. Addn. of NaCl and AcOH to heated latex (1:9) causes flocculation but not coagulation. On the other hand, EtOH and alum are coalescing agents (cf. *C. A.* **19**, 419), their action being similar to that of thymol and of β-naphthol (cf. *C. A.* **20**, 676–7). **VI. Some further observations on B mixture.** *Ibid* 527–33. (In English 534–6.)—Further data (cf. *C. A.* **19**, 419) show the changes brought about by heating dild. latex, repeated extn. of the coalase and the influence of mech. factors on coalescence. Serum from fresh dild. latex coagulated with AcOH gives when heated a flocculent ppt., whereas serum from heated latex remains clear, showing that heating destroys the coalase. On exposure to air, the sera both from fresh and from heated latex become turbid and form gelatinous decompn. products. When these are filtered, and the new sera are again heated, the same phenomenon occurs, a ppt. being obtained from the serum of fresh latex, while the serum from heated latex remains clear. This indicates that the N compds. not coagulated by AcOH but pptd. on heating in acid medium do not serve as nutrient for the microörganisms which cause the pptn. in very dil. serum. Rubber obtained from coagulation with AcOH from fresh dild. latex contains less N than that from heated dild. latex (averaging 0.354 and 0.411%, resp.), because of pptn. of N compds. in the latter. The coagulum of B mixt. coalesced with fresh latex gives an ext. with aq. Na₂CO₃ which has the power of coagulating more B mixt., which lends support to the enzyme (coalase) theory in opposition to the chem. theory (cf. Belgrave, *C. A.* **20**, 1921). The rate of coalescence is influenced by phys. factors, such as the shape of the receptacle used for coagulation. Thus the narrower and thicker the flocculated layer the greater the upward pressure and the more rapid the coalescence.
C. C. DAVIS

Cable coverings resistant to abrasion and to decomposition by heat. WERNER ESCH. *Kautschuk* **1927**, 285; cf. *C. A.* **21**, 2818.—The addn. of "Vandex" (Se) to rubber mixts. for cable coverings not only increases their resistance to abrasion but also makes them particularly resistant to the deterioration by heat which is characterized by softening and tackiness.
C. C. DAVIS

Cable coverings resistant to abrasion and the VDE specifications. R. APT. *Kaut-*

schuk **1927,** 316.—Comments on an article by Esch (cf. preceding abstr.).   **Reply.**
WERNER ESCH.   *Ibid* 316.   C. C. DAVIS

The constitution of rubber.   RUDOLF PUMMERER.   *Z. angew. Chem.* **40,** 1168–72
(1927).—See *C. A.* **21,** 3765.   C. C. DAVIS

Specifications for rubber goods and the value of performance tests.   J. M. BIERER
AND C. C. DAVIS.   *Trans. Inst. Rubber Industry* **3,** 151–84(1927).—Present specifications
for the purchase of rubber goods, including those of the U. S. government, the railroads
and the cities, are fundamentally wrong, and in spite of elaborate phys. and chem.
requirements, not only fail to assure the purchase of satisfactory goods but actually
prevent the purchase of serviceable goods in the most economical manner.   The paper
is an indictment of specifications of this type, an indictment which is all the more justi-
fied because of the recent development of performance tests and of improved methods
of compounding which warrant sweeping changes in specifications.   In support of the
argument that those who purchase rubber goods by specification are neither aiding nor
encouraging phys. and chem. developments and are not even taking advantage of what
is known, recently developed tests for imitating service conditions, such as *abrasion
tests, flexing machines,* the *O-aging test,* and such adjuncts as *reclaimed rubber* and *anti-
oxidants,* are discussed.   All of these developments are ignored by the writer of specifi-
cations, and at present there is general confusion and extravagance in the purchase of
goods.   In conclusion a plan is suggested for rectifying the extravagance and ignorance
now prevailing.   Incidental to the theme and in connection with developments of value
to the writer of specifications, new data on the *relative resistance to abrasion of various
types of rubber mixts.* on 7 abrasion machines, the *variation in the resistance to flexing
of rubber belts* and in the *"friction test" with the time of vulcanization,* the *relation between
"friction test" and resistance to flexing,* the *relation between the "friction test" and the
tensile properties,* the formulation of *rubber mixts. highly resistant to heating,* the *relative
activity of com. antioxidants* under different conditions, and the *"liquefaction" (defloccu-
lation) by solvents of stiff pastes prepd. from powders and liquids.*   Tests of 5 widely
different rubber mixts. show that the relative resistance of different mixts. varies so
greatly with the type of app. that the choice of any app. depends entirely upon the type
of abrasion to be imitated.   The "friction test" gives a false indication of the life of a
belt, whereas the flexing test more nearly approaches service conditions.   The flexing
test does not duplicate service conditions because the hysteresis cycles are much more
frequent and the residual temp. is higher, while the "friction test" does not involve
repeated stretching and hysteresis losses and so has no relation to service conditions.
Both the "friction" strength and the tensile properties increase to a max. and then
decline with increase in the time of cure, but in quite different ways, so that no relation
is evident.   Mixts. contg. alkyl thiuramdisulfides but no S are extraordinarily resistant
to heating and a mixt. of smoked sheets 100, tetramethylthiuramdisulfide 2, ZnO 10,
C black 25, may be vulcanized 8 hrs. at 142° and its elongation and tensile strength
still be about the same as they are after a cure of only 0.5 hr. at 142°.   In their resis-
tance to prolonged heating, such mixts. are far superior to similar mixts. contg. S and
less active accelerators, and they also have satisfactory aging properties.   Org. acceler-
ators not only improve the properties of cured rubber and increase the economy of
vulcanizing, but improve aging and increase the range of cure over which rubber ages
well.   Antioxidants have a far greater power of retarding deterioration, but may at
the same time be accelerators, so that a powerful accelerator which improves the aging
cannot be regarded as fundamentally different from an antioxidant which is powerful
where the other is weak, and *vice versa.*   They must therefore be classified according
to their predominant characteristic.   The com. important antioxidants, *"Agerite"*
(aldol-α-naphthylamine), *"Antox"*   (a mixt. of p-HOC$_6$H$_4$NH$_2$ and BaSO$_4$) and
"V.G.B." (a condensation product of AcH and PhNH$_2$Cl) were compared in different
proportions in a base mixt., cured to different degrees, by aging in O under 300 lb.
per sq. in. pressure at 70° for various lengths of time.   The results show that (1) in small
proportions one antioxidant may be considerably more effective than another, whereas
in larger proportions they become approx. the same in their action, and that (2) even
when a rubber mixt. contains an antioxidant, its deterioration may be comparatively
rapid when overcured, *i. e.,* contrary to widespread belief, antioxidants are not particularly
effective in retarding deterioration in an overcured mixt.   By the aid of antioxidants,
it is possible to retard the rapid deterioration caused by Cu compds., in illustration
of which data show that p-HOC$_6$H$_4$NH$_2$ is extraordinarily effective against CuI.   Thus
a mixt. contg. 0.3% CuI (based on the rubber) but no p-HOC$_6$H$_4$NH$_2$ became after
10 months inelastic and very weak, whereas a similar mixt. with 0.75% p-HOC$_6$H$_4$NH$_2$
was practically unchanged.   Other antioxidants are more effective than p-HOC$_6$H$_4$NH$_2$
in the absence of Cu compds. but fail to protect rubber when Cu compds. are present,
and in general a powerful antioxidant action in the absence of Cu does not indicate a

protective action in its presence. Since the influence of *reclaimed rubber* on the phys. properties of cured mixts. may depend in part upon its ability to wet the pigments and increase their dispersion, expts. are described to illustrate by analogy the action which may play a part, a liquid medium representing the rubber matrix. If ZnO is mixed with kerosene, turpentine, xylene or other suitable liquid so that the paste can be kneaded without either flowing or crumbling, and a very small proportion (*e. g.*, 2% by wt. of the ZnO) of the acetone-sol. part of certain reclaimed rubbers is rubbed into the paste, the latter immediately becomes thin enough to pour. Each powder requires a different proportion of liquid to paste, but as an indication 10 g. of ZnO, C black, whiting, barytes or china clay require about 10, 25, 6, 2 and 10 cc., resp., of kerosene to make a paste suitable for the demonstration. A ZnO-kerosene paste may also be "liquefied" by similar small proportions of the acetone-sol. component of raw rubber, degras, palm oil, oleic acid, stearic acid, rosin, pine tar, asphalt, etc. A particularly large no. of agents liquefy ZnO pastes, but pastes of some materials, notably C black, are much less readily lique-fied. Degras has a thinning action on a C black-kerosene paste, and one of the most striking cases is the liquefaction of a C black-water paste by Na oleate, a 2:5 paste being liquefied by 8% (based on the C black). There is a min. proportion of thinning agent to powder below which liquefaction does not take place. This min. varies with each combination, *e. g.*, it is 0.3% stearic or oleic acid by wt. of ZnO. The min. is, moreover, practically independent of the particular liquid and the proportion of the latter used in making the paste. It is possible by a suitable thinning agent to liquefy pastes of any of the ordinary rubber compounding ingredients, such as C black, ZnO, whiting, clay, lithopone, slate, barytes, Mg carbonate, lime, litharge, red Fe oxide, etc. There are many rubber mixts., including nearly all those in specification goods, where the quality desired can be obtained by new rubber alone or by a mixt. of new and reclaimed rubber. Therefore specifications which forbid the use of reclaimed rubber may make impossible the production of goods in the most economical manner, and it is of great importance that large consumers such as the U. S. Government recognize the proper place of re-claimed rubber in specification goods. A general discussion follows the paper.

C. C. Davis

Methods for the purification of rubber hydrocarbons. Rudolf Pummerer and Hermann Miedel. *Ber.* **60B**, 2148–52(1927).—Methods of purification which have been described up to the present time are of 4 types: (1) extn. with acetone (Harries); (2) fractional pptn. (cf. P. and Koch, *C. A.* **18**, 3737); (3) purification with alkalies (cf. P., *C. A.* **20**, 2429); and (4) fractional soln. (cf. P. and Koch, *C. A.* **18**, 3737; Feuchter, *C. A.* **19**, 2576). Method (1) gives products, the compn. of which conforms much more closely to the theoretical value than does that of the raw material, but which still con-tain proteins and sugar. Method (2) gives a ppt. which contains 30–40% of the original rubber and the major part of the non-rubber components. The supernatant soln. yields a product which conforms in its analyses to the theoretical value, but which still contains N, and which gives a turbid soln. in hexahydrotoluene. To investigate this latter problem further, the product was purified by adding the pptg. agent until the soln. became turbid, which resulted in a few hrs. in the sepn. of 2 layers, a concd. lower layer and an upper more dil. layer. To each layer was added excess pptg. agent, and in each case pptn. again occurred. The ppts. were then subjected to the same treatment again, solvent, pptg. agent, concn. and temp. being varied to det. the best conditions. Petroleum ether was found to be the best solvent and acetone the best precipitant. Smoked sheet and crepe furnished relatively pure products which gave clear solns. in hexahydrotoluene, but neither smoked sheet nor crepe, even after 8 fractiona-tions, gave a product free of N. Method (3) utilizes KOH in MeOH, and it is possible to remove by this means all N compds. and acids, but the residual KOH can be quant. removed only in expts. on the smallest scale and then only with great difficulty. Though in the fractional soln. method of Feuchter (*C. A.* **19**, 2576) the gel skeleton insol. in Et₂O and contg. the impurities was considered to be of no importance, it is probably of great interest and expts. are in progress to det. its nature.

C. C. Davis

The preparation of pure rubber from latex by means of alkali, and its separation into sol-rubber and gel-rubber. Rudolf Pummerer and Hans Pahl. *Ber.* **60B**, 2152–63(1927).—The product obtained from NaOH treatment of the latex, the prepn. and properties of which have already been described (cf. *C. A.* **20**, 2429), may be termed total *rubber* ("Totalkautschuk"). Its intimate 2-phase structure plays an important part in the characteristic elasticity, viscosity and crystn. of rubber. Röntgenographic interferences are very distinct in total rubber, gel-rubber and sol-rubber. Gel-rubber absorbs 1 mol. of I per C₅H₈ unit. When total rubber is plasticized until no longer elastic, the gel-rubber probably becomes sol. in the warm sol-rubber, but on the other hand gel-rubber can be plasticized until devoid of elasticity and it then becomes sol. in Et₂O. The diffusion of rubber in Et₂O observed by Feuchter (*C. A.* **19**, 2576) shows

no definite end point as was assumed at first, for on continued treatment gel-rubber continues to pass into soln. Cumene was the best solvent found for gel-rubber. Nevertheless gel-rubber is not identical with sol-rubber, but is probably simply a disaggregated component of the latter. The relative quantities of sol-rubber and gel-rubber in total rubber is still in doubt, but an expt. with exclusion of air indicated about 35%. From total rubber and from sol-rubber were prepd. by treatment in $CHCl_3$ with HCl the corresponding *hydrochlorides*, both probably of the compn. $(C_5H_9Cl)x$. From rubber and $C(NO_2)_4$ immediately formed a yellow *compd.* In hexahydrotoluene at $0°$, rubber and $C(NO_2)_4$ formed a yellow soln. which after 5–6 days became colorless and pptd. a 90–95% yield of a pale yellow or rose colored *addn. compd., rubber tetranitromethanate,* perhaps of the compn. $-C-C-$. Not all of the double bonds of the rubber reacted

$$O:NO \quad C(NO_2)_3$$

with $C(NO_2)_4$ to form this compd. with raw rubber and with gel-rubber 5 isoprene units combining with 1 $C(NO_2)_4$ unit, and with sol-rubber 6 isoprene units. This does not, however, indicate that sol- and gel-rubbers are chem. different, because of the colloidal conditions existing. The rubber tetranitromethanates were fine amorphous powders insol. in all cold org. solvents, and adsorbed Br. They gave opalescent solns. in warm $PhNO_2$ or $PhNH_2$, from which sepd. on heating flocculent *decompn. products.* The tetranitromethanates turned yellow at about $150°$, brown at about $175°$ and ultimately charred. A study of the reaction between rubber and $C(NO_2)_4$ up to $75°$ showed that even with a large excess of $C(NO_2)_4$ the reaction always resulted in the tetranitromethanate. Above $75°$ decompn. ensued, with evolution of N oxides. *Comparative vulcanization tests of purified rubbers and raw rubber* showed a close similarity in the rate of vulcanization and in phys. properties when cured with 10% S, indicating that ordinary soft vulcanized rubber owes its properties to the pure rubber hydrocarbon. On the other hand sol-rubber and gel-rubber failed to vulcanize with 7.5% S even after 210 min. at 3.5 atm. steam pressure, and most of the S was still extractable with Me_2CO. The *elec. insulating power of hard rubber* prepd. from purified rubber with 30% S was 3 times as great as the corresponding hard rubber from crepe. C. C. DAVIS

The absorption of rubber and of gutta-percha in the ultra-violet spectral region. GÜNTHER SCHEIBE AND RUDOLF PUMMERER. *Ber.* 60, 2163–7(1927).—The absorption measurements were made in pure hexahydrotoluene solns. of rubber, since this solvent is transparent in the extreme ultra-violet region. The method was that of Scheibe, May and Fischer (*C. A.* 19, 609; Rössler, *C. A.* 21, 1228). The absorption curves of rubber of different degrees of purity, including rubber from latex treated with NaOH, rubber from non-coagulated latex and sol-rubber were the same from log $k = 4$ to log $k = 2$, but below about log $k = 2$ the curves became very different, that of sol-rubber deviating least below log $k = 2$ from its course over the range from log $k = 4$ to log $k = 2$. The curve of sol-rubber is probably most nearly that of the rubber hydrocarbon. Curves of the *absorption of diallyl, trimethylethylene, dimethylbutadiene and isoprene* are shown for comparison. This comparison shows that the Harries formula of rubber conforms to the optical properties. Earlier expts. by P. and Burkard (*C. A.* 17, 898) on the *hydrogenation of rubber* showed that rubber combines with H only in very dil. solns. of hexahydrotoluene, suggesting that a change in the double bonds occurred. Optical examn., however, indicated that the no. of double bonds of rubber in soln. was the same whether it could or could not be hydrogenated. *Purified gutta-percha* in hexahydrotoluene gave the same absorption curve as rubber so that the no. and the character of the double bonds of each substance must be the same. A comparison of sol-rubber, gel-rubber and "total" rubber (cf. preceding abstr.) showed a stronger absorption in the lower part of the absorption curve of gel-rubber, which is related to its pale brown color. The curves were otherwise identical. C. C. DAVIS

Cryoscopic molecular weight determinations of rubber. RUDOLF PUMMERER, HILDE NIELSEN AND WOLFGANG GÜNDEL. *Ber.* 60, 2167–75(1927).—Contrary to Staudinger, who considers that macromols. of rubber contain 100–1000 isoprene units, a parent hydrocarbon with a marked tendency to associate leads to mols. of enormous wt. In this case the problem of chem. valence and structure is directly related to colloid chem. and crystallographic problems. An association through secondary valences of the character suggested must be reversible, but it is improbable that the macromol. of Staudinger could dissociate in soln. The results of ultra-violet absorption measurements (cf. preceding abstr.) and the relatively high stability of rubber in soln. toward I without a catalyst and in the absence of air both preclude the possibility of tervalent C. In view of earlier hydrogenation expts., which indicated a parent mol. with a mol. wt. of 600–700, the mol. wt. of rubber in camphor was next investigated. Films of rubber were prepd. by completely evapg. *in vacuo* on the walls of a tube at $50°$ a soln. of rubber, and then dissolving directly by admission of fused camphor. This technic

gave different results from those obtained by dissolving rubber in camphor, which caused swelling and an apparent soln., the mol. wts. then being very high. At concns. of 1:4 and 1:10, samples of purified rubber, including diffused rubber from latex and crepe, rubber purified by alkali, sol-rubber and gel-rubber showed mol. wts. of 1100–1600. With benzylidenecamphor the mol. wts. were 1400–2500. At concns. of 1:50 in menthol, values of 1200–1600 were obtained. On diln. to 1:100, the mol. wts. were only about 0.5 as great, indicating extensive disassociation. Further diln. did not cause a further decrease in mol. wt. The lowest values for sol-rubber, gel-rubber, and diffused rubber were 520–620, while calcns. based on 8, 9 and 10 isoprene units indicated 544, 612 and 680, resp. The results indicate 8 isoprene units, though the expts. do not warrant the acceptance of this as an established fact. It is of great significance that the rubber fractions which differ so much in soly. show the same av. mol. wt. in camphor and in menthol. Their essential difference must therefore lie in their different powers of aggregation. The action of O_3, the light-absorption values and the extraordinary tendency toward cyclization are most readily explained by a *ring structure*. *Hydro-rubber* and *cyclo-rubber* also showed a mol. wt. around 600, whereas a partially hydrogenated and a partially cyclized rubber showed values of 1583 and 1442, resp. Under certain conditions a stable "double mol." probably exists, rendering it more difficult still to draw reliable conclusions concerning the mol. wt. of rubber. C. C. D.

Studies on Hevea latex. VII. Rubber derived from preserved latex. R. O. BISHOP. *Malayan Agr. J.* **15**, 271–82(1927); cf. *C. A.* **21**, 2575.—In view of the results obtained by other investigators on the variable rate of vulcanization of rubber from latex preserved with NH_4OH (cf. de Vries, Riebl and Beumée-Nieuwland, *C. A.* **19**, 2282), the problem was studied with the object of detg. the cause of the variation. Latex which had already been preserved with 1% NH_4OH (cf. *C. A.* **21**, 1900) was coagulated with EtOH and with AcOH, resp., and the rubber converted into crepes. Vulcanized in rubber-S mixts., the crepe from AcOH coagulation behaved in a manner similar to that reported by de V. and B.-N. (*loc. cit.*), while the crepe from EtOH coagulation vulcanized at a more rapid rate. It is probable that a natural accelerator is liberated by the NH_3 and is entrained in the rapidly formed coagulum with EtOH but not in the more slowly forming coagulum with AcOH. The known rhythmical changes with time in the rate of vulcanization of rubber from latex preserved with NH_4OH are not a result of hydrolysis of proteins to an accelerator, for detns. of the amino N in alk. latex showed no evidence of gradual hydrolysis. Similar detns. of latex contg. NaOH, in which hydrolysis should be greater, also failed to indicate the formation of amino N during any hydrolysis of proteins. Detns. of *amino acids in preserved latex serum of different ages* further showed that there is no rapid development of amino acids from the proteins of the serum which is at all commensurate with the changes in the rate of vulcanization. Similar detns. of the *changes in the amino-acid content of preserved latex* again showed no increase of amino acids with age which could be held responsible for the observed increase in the rate of vulcanization. Since the rapid initial increase in the rate of vulcanization is not caused by the formation of accelerators from the proteins, it is possible that a *thermolabile complex* such as that suggested by Belgrave (cf. *C. A.* **20**, 1921; B. and Bishop, *C. A.* **18**, 3738) is sensitive to changes in the p_H value of the latex and therefore governs the rate of vulcanization. If the complex is a phosphatide, the changes in this ratio are detd. by changes in the fatty acids. If such a labile phosphatide is present, it is also of importance in connection with the vulcanizing properties of rubber coagulated at different p_H values with EtOH observed by B. (*C. A.* **19**, 418) and the effects on rubber of the oxidation of its fatty acids (cf. Whitby, Dolid and Yorston, *C. A.* **20**, 3099; van Rossem and Dekker, *C. A.* **21**, 195).

C. C. DAVIS

Conversion of rubber into thermoplastic products with properties similar to gutta-percha, balata and shellac. I. Methods of preparation and general properties. H. L. FISHER. *Ind. Eng. Chem.* **19**, 1325–8(1927).—When raw rubber is heated with any one of numerous sulfonyl or sulfonic compds. it is converted into substances which differ widely in phys. characteristics from the raw rubber. Unlike products of vulcanization, these products have the same empirical compn. as the original rubber, in all cases analyses indicating $(C_5H_8)x$. Not only do they differ physically from the original rubber, but their phys. properties vary with the conversion agent and its concn. and with the time, temp. and other conditions of heating. In general they resemble gutta-percha, balata, or shellac and with the term *"thermoprene"* as a basis, these 3 general types are designated *thermoprene-GP*, *thermoprene-HB* and *thermoprene-SL*, resp. When from the large no. of compds. capable of converting rubber into products resembling gutta-percha, balata or shellac, those not economical and not convenient to handle are eliminated, there remain compds. such as p-$HOC_6H_4SO_2H$, p-$MeC_6H_4SO_3H$ and p-$MeC_6H_4SO_2Cl$ with which products of great com. value can be formed, *e. g.*, for molded

articles, elec. insulation, paints, adhesives, and above all for binding rubber to metals according to the Vulcalock process (cf. *Canadian Patent* 256,797(1925)). Thus on heating rubber in sheet form with 10% by wt. of an org. sulfonyl chloride or sulfonic acid for several hrs. at 125–35°, thermoplastic products resembling gutta-percha or balata are obtained. Heated under similar conditions but in bulk, the reaction is exothermic and the products resemble shellac, and in general when the proportion of agent is high enough for the reaction to be exothermic, the product is hard and resembles shellac. Rubber and 7.5% of p-HOC$_6$H$_4$SO$_3$H give products like gutta-percha, which are sol. in C$_6$H$_6$, are good adhesives and are the basis of the Vulcalock process. Heated with 5% of H$_2$SO$_4$, rubber gives products resembling balata. The thermoplastic products can be vulcanized with S (see following abstr.). **II. Chemistry of the reaction.** H. L. FISHER AND E. M. McCOLM. *Ibid* 1328–33.—A detailed study of the chem. properties of the thermoplastic products and of the reaction already described, particular attention being paid to thermoprene-SL products, which are sol. in org. solvents. When purified, the chief component is a hydrocarbon of the same empirical formula (C$_5$H$_8$)x as rubber, so that the reaction is probably an *isomerization*. It is 55–60% as unsatd. as the original rubber hydrocarbon. The thermoplastic products combine with S to form hard products which are no longer thermoplastic and are insol. in org. solvents. Since they are less unsatd. than the original rubber, they combine with less S, 21% (corresponding to 57% of the unsatn. of the original rubber) being the max. combined S obtained. With HCl and HBr thermoprene-SL forms *HCl- and HBr-addn. compds.*, which are not thermoplastic. Thermoprene-SL products can be halogenated with Br and with I, and are oxidized by air, O$_3$, perbenzoic acid, KMnO$_4$ and H$_2$O$_2$, in one case air giving an *oxidation compd.* of the compn. C$_{10}$H$_{16}$O, and perbenzoic acid giving the *compd.* (C$_5$H$_8$O)x, the products from the other oxidizing agents being less definite. The purified chief component of thermoprene-SL could not be hydrogenated with H under pressure and a catalyst, but can be nitrated by HNO$_3$, forming a *compd.* of the approx. compn. C$_5$H$_7$NO$_2$. When heated, thermoprene-SL is more stable than the original rubber, almost no evolution of volatile products occurring up to 350°. Rubber was heated with numerous other inorg. and org. compds., of the most varied types, a complete list of which is given to det. whether other interesting and valuable products are formed. In no case, however, were the products like the thermoprenes already described. C. C. DAVIS

Variation in plantation rubber. B. J. EATON AND R. O. BISHOP. *Malayan Agr. J.* **15**, 283–9(1927).—The collection at the Malayan Exhibition of samples of plantation smoked sheet and crepes from the best estates gave an opportunity for detg. the rate of cure in a rubber-S (90:10) mixt. and the phys. quality after curing at 140° of rubber which represented the best com. products. All samples of smoked sheet were of excellent tensile strength, but 18 out of 24 samples had optimum times of cure of 195–240 min., whereas the normal time under the same conditions is 150–165 min. No certain reason could be assigned, for 17 samples were prepd. with AcOH and only 2 with HCO$_2$H, and those from HCO$_2$H had the slowest rate of vulcanization. All samples of pale crépe vulcanized at about the same rate (the majority from 180 to 210 min. for optimum cure) and the differences in tensile strength were small. Samples of "compo" crepe differed little in tensile strength, and in general they vulcanized more rapidly than the smoked sheets. Unsmoked sheets were equal in quality to smoked sheets but varied considerably in their rate of vulcanization (150–210 min. for optimum cure). The results indicate that in the best com. rubber, particularly in smoked sheets, there is considerable variability in the rate of vulcanization, while the phys. properties in the cured state are fairly uniform (cf. de Vries, *C. A.* **21**, 1567). The samples which won prizes for excellence of appearance and superficial quality were no better than those of slightly less desirable visible aspect. C. C. DAVIS

Magnesium compounds and their use in the rubber industry. E. BRUCE WARREN. *Rubber Age* (London) **8**, 443–5(1927).—A general description. C. C. DAVIS

The preservation of rubber. A survey of progress based on the patent literature of the past year. ALADIN. *Gummi-Ztg.* **42**, 644–5(1927).—Numerous patents are itemized and their character is briefly described. C. C. DAVIS

The testing of rubber goods. ANON. Bur. of Standards, *Circular* No. 38, 81 pp. (1927).—The circular describes the methods of collecting raw rubber, the raw materials and processes employed in the manuf. of various types of rubber goods, methods of testing soft and hard rubber, including a comparison of normal and accelerated aging, tests of the phys. properties, with the influence of temp. and other factors, methods of chem. analysis, various testing app., the standard procedure of phys. and chem. tests of the Federal Specification Board, a list of Bur. of Standards publications on rubber and a bibliography of 19 books on rubber. C. C. DAVIS

Brown factice in rubber mixtures. K. HOLZNER. *Gummi-Ztg.* **42**, 593(1927).—

Brown factice is not inferior to white factice if properly manufactured and used, and unfavorable results, particularly in its aging effect, can usually be traced to factice with a high oil content.   C. C. DAVIS

The effect of Emarex (M. R. X.) on the physical properties of a vulcanizate. L. STOLL. *Gummi-Ztg.* 42, 695–6(1927).—A base mixt. of smoked sheet 100, S 5, diphenyl-guanidine 1.5, ZnO 5 and M. R. X. 5–50 was vulcanized at 3.2 atm. steam pressure for different times, the same technic being employed as in previous work (*C. A.* 20, 843). Five parts of M. R. X. had a distinct accelerating action, extended the range of optimum cure and did not impair the tensile properties. This accelerating effect was the same as an increase of diphenylguanidine to 2 parts in the mixt. contg. no M. R. X., or as an increase of cure to 3.9 atm. pressure of this base mixt. The elongation at the optimum cure increased with the proportion of M. R. X. up to 30 parts, above which it decreased. The permanent elongation increased and the hardness diminished with increase in the proportion of M. R. X.   C. C. DAVIS

Vulcanization accelerators and their comparative effect in hard rubber mixtures. RUDOLF DITMAR. *Chem.-Ztg.* 51, 901–2; *India Rubber J.* 74, 1000(1927).—The comparative results obtained with soft vulcanized rubber (cf. *C. A.* 21, 1567) are not true for hard rubber. At 100° it was not possible to obtain hard rubber with any accelerator in mixts. of crepe 100, S 50, C black 40, beeswax 5, PbO 20, accelerator 2, but at 143° some accelerators, *e. g.*, tetramethylthiuramdisulfide, gave satisfactory products at a cure of 90 min. In general when PbO was replaced by ZnO, the accelerators which gave satisfactory hard rubber with PbO failed to cure the same mixts. with ZnO, and *vice versa*. By replacing PbO or ZnO by lithopone and beeswax by carnauba wax, satisfactory hard rubbers were obtained with some accelerators at a cure of 60 min. at 143°. On the other hand some accelerators, *e. g.*, tetramethylthiuramdisulfide, which were among those which gave particularly good results with ZnO, actually retarded the rate of cure when ZnO or PbO was replaced by lithopone.   C. C. DAVIS

Tire fabrics from the rubber manufacturer's viewpoint. A. M. MUNRO. *Textile J. of Australia* 2, 263–5, 319–20, 375–7(1927).   CHAS. E. MULLIN

Dark green, metallic spots on colored chrome leather women's shoes, caused by transparent rubbers vulcanized with sulfur chloride. RUDOLF DITMAR. *Gummi-Ztg.* 42, 533(1927).—The observation that transparent rubbers caused spots on chrome shoe leather is attributed to the decompn. by water of residual traces of S_2Cl_2 to HCl. The HCl then liberates CrO_3 from the chromates, and by oxidizing the rubber the CrO_3 is reduced to lower Cr oxides which are responsible for the characteristic metallic green spots. This effect can be avoided by treating the vulcanized rubbers with NH_3, by absorption of a colloidal dusting agent (cf. *C. A.* 21, 510) or by discontinuing the S_2Cl_2 process in favor of hot vulcanization.   C. C. DAVIS

Results of research on South African rubber. ERICH NEUFELD. *Kautschuk* 1927, 359–64; cf. *C. A.* 21, 1373.—An investigation was made of the com. value of the rubber from *Euphorbia grandidens, tetragona* and *triangularis*, trees which abound in Africa. Various samples of latex contained 10.33–30.1% rubber, 23.24–65.5% resins and 36.03–61.80% water. The latex of *Euphorbia tirucalli* and *dregeana* contained only 8.3 and 16.2% rubber resp., and were not investigated further. The latex of *E. grandidens, tetragona* and *triangularis* tended to coagulate spontaneously and required immediate addn. of NH_4OH, HCHO, H_3BO_3, α-naphthol or casein soap. It was preserved best with dil. NH_4OH or aq. HCHO. After extn. with Me_2CO or EtOH the rubber was dark brown and only slightly tacky. The rubber, still contg. 5–6% resins, was tested in comparison with plantation crepe by partial replacement of the latter in several representative formulas. It was found that there was no practical change in the quality when 20–25% of first latex crepe was replaced by *Euphorbia* rubber. The extd. *Euphorbia* rubber is considered about 80% as good as the best plantation rubber. The resin of *Euphorbia* rubber contains cholesterol and a small proportion of org. acids. Its chief component is a hard resin which m. 80–100°, with a smaller quantity of a soft resin. Both are optically active (dextro), unsaponifiable and very good for *varnishes*. On distn. the resins yielded turpentine oil, rosin oil and other common derivs. of such distns. Since the coagulum from *Euphorbia* latex contains only 25% rubber and so much resin, its economic value depends upon the utilization of its resin component.
                                                                          C. C. DAVIS

The colloid chemistry of rubber latexes. III. Individual forms of the rubber particles in latex and their inheritable properties. E. A. HAUSER. *Kautschuk* 1927, 357–9; cf. H. and Scholz, *C. A.* 22, 511.—Expts. are described in which it was attempted to correlate the characteristic shape and size of latex particles from different trees with their origin (cf. Bobilioff, *C. A.* 14, 1063; Freundlich and H., *C. A.* 19, 2280). The expts. also indicate that there are 2 general types of latex, one in which the particles vary

relatively little in size (0.5–1.5μ), and the other where there is relatively wide variation (0.5–$4.0\ \mu$). Photomicrographs are shown. C. C. D.

New principles in the compounding of rubber mixtures. I. WERNER ESCH. *Caoutchouc & gutta-percha* **25**, 13844–7(1928).—See *C. A.* **22**, 511. C. C. DAVIS

A hardness tester for rubber. E. C. ZIMMERMAN AND R. W. BROWN. *Ind. Eng. Chem.* **20**, 216–8(1928).—The instrument which is described and illustrated is of the penetrometer type, and may be of portable or mounted form. It overcomes several shortcomings of earlier types, notably in that the rubber is under a predetd. definite pressure and the instrument is aligned with the surface which is compressed.

C. C. DAVIS

Brittleness tests for rubber and gutta-percha compounds. G. T. KOHMAN AND R. L. PEEK, JR. *Ind. Eng. Chem.* **20**, 81–3(1928).—From a practical point of view, brittleness may be regarded as a tendency to fracture under moderate but sudden deformation. On this basis, an app. and technic were developed for measuring the *highest temp. at which a material will fracture* under standardized conditions. With the technic employed, the min. temp. at which fracture did not occur was for pale crepe —58°, smoked sheet —57°, pure rubber hydrocarbon —55°, gutta-percha —28°, vulcanized rubber —53° and balata —44°. This indicates that each substance has a characteristic temp. below which it becomes brittle, and that it should not be subjected to mech. stress below this temp. This crit. temp. is independent of the conditions of the test and is unaltered even when the substance is under great hydrostatic pressure, so that a change in the intimate structure of the substance probably occurs, a change of phase perhaps being involved (cf. Park, *C. A.* **19**, 1209; Hock, *C. A.* **19**, 3036; LeBlanc and Kröger, *C. A.* **20**, 2431). C. C. DAVIS

The aging of rubber. F. JACOBS. *Caoutchouc & gutta-percha* **24**, 13762–5, 13802–4 (1927); cf. *C. A.* **21**, 2816, 3489.—A survey of the views of various authors on the phenomena of aging. C. C. DAVIS

Effect of certain metallic salts on the aging of a tread compound. B. S. TAYLOR AND W. N. JONES. *Ind. Eng. Chem.* **20**, 132–3(1928).—The influence of very small proportions of cupric stearate (0.001–0.5%), manganic oleate (0.1–1.0%), ferric stearate (0.1–0.5%) and mercuric stearate (0.1–1.0%) on the deterioration of a rubber-S-ZnO-gas black-accelerator mixt. was detd. by aging in O under 300 lbs. per sq. in. pressure at 70° and in air at 70°. The base mixt. was also aged after surface treatment with $CuCl_2$ soln. Judged by the O-aging test, 0.1% or more of cupric stearate, 0.1% or more of manganic stearate, 0.5% ferric stearate or surface treatment with $CuCl_2$ greatly hastens deterioration, whereas even 1% mercuric stearate does no harm. The phys. effects of the O-aging and of the aging in air differed notably, heating with compressed O causing hardening and brittleness and heating in air causing a weakening with little change in flexibility. The effect of surface treatment with $CuCl_2$ is at variance with the results of Williams (*C. A.* **20**, 2093). No data are given to correlate these diverse effects with the natural aging of the various mixts. C. C. DAVIS

Comments on antioxidants and rubber. G. BERNSTEIN. *Rev. gén. caoutchouc* **1927**, No. 37, 3.—Polemical (cf. Moureu and Dufraisse, *C. A.* **22**, 511). C. C. DAVIS

The problem of the transformation temperature of rubber lying from about 60° to 80°. L. STOLL. *Gummi-Ztg.* **42**, 745–6(1927).—In view of the accumulating evidence that rubber undergoes some sort of internal transformation in the temp. range of 60–80°, the literature contg. evidence on this subject is reviewed. Numerous references are included. C. C. DAVIS

Formulas of [rubber] mixtures. RUDOLF DITMAR. *Caoutchouc & gutta-percha* **24**, 13814–5(1927); **25**, 13849–50(1928); cf. *C. A.* **21**, 2817. C. C. DAVIS

Value of the rubber hydrocarbon in reclaimed rubber. W. W. VOGT. *Ind. Eng. Chem.* **20**, 140–3(1928).—In detg. the quality imparted to a representative mixt. of the tire-tread type by different proportions of reclaimed rubber, it was essential to maintain the compn. of the mixts. unchanged except for the replacement of new rubber by an equiv. wt. of reclaimed rubber hydrocarbon. Accordingly as the alkali whole tire reclaim was added in increasing proportion, the ingredients which were present in the base mixt. and in the reclaim were reduced to compensate for the addns. The cures were also adjusted by the addn. of decreasing proportions of PbO with increase in the reclaim, so that the technically optimum cure was the same for the series. A comparison of tensile properties and resistance to abrasion (by 5 methods) showed that as more and more new rubber was replaced by reclaimed hydrocarbon, the quality became poorer, and therefore that the reclaimed hydrocarbon was inferior to new rubber hydrocarbon. The relative stiffness of mixts. with and without reclaim depended upon the part of the stress-strain curve chosen for comparison, reclaim increasing the stiffness at low elongations (*e. g.*, 200%) and decreasing it at higher elongations (*e. g.*, 500%). The results emphasize the fact that any method of compounding which involves direct substitution

of reclaimed hydrocarbon for new rubber hydrocarbon without further compensation or adjustment of other ingredients will give inferior quality. Four methods besides the Williams method for testing resistance to abrasion are described. C. C. Davis

Factors in processing reclaimed rubber. P. S. Shoaff. *Ind. Eng. Chem.* **20**, 152–5(1928).—The production of reclaimed rubber of uniformly good quality cured and uncured depends not only upon the process used for devulcanizing but upon the judicious choice and blending of the raw material. The time of devulcanization is a min. when the material is ground to a uniform state of subdivision without an excessive proportion of fine material, for the latter becomes too soft and lowers the av. quality. Moreover fine material is to be avoided because of the expense of its recovery from the spent and wash liquors. In general the higher the temp. of devulcanization to obtain a reclaim of a particular character, the lower is its tensile strength and the higher is its elongation after curing. It is considered that the use of softeners should be minimized and that their choice should depend upon the aging properties which they impart rather than upon their plasticizing action. NaOH should be reduced to 0.1% by washing, as judged by boiling 10 g. for 4 hrs. in water and titrating. A total alky. detn. requires 48 hrs.' boiling. To avoid tackiness, the final drying temp. should not exceed 300° F. During the final milling, the reclaim should be at 140–160° F. and during refining at 165–185° F., for the use of higher temps. gives products of poorer quality when cured. The operation of different types of equipment and future developments are discussed.

C. C. Davis

Rate of cure of reclaimed rubber. N. A. Shepard, H. F. Palmer and G. W. Miller. *Ind. Eng. Chem.* **20**, 143–52(1928).—In detg. the rates of vulcanization of different mixts., the time required for a mixt. to reach a max. stress at a given intermediate elongation was chosen as a basis of comparison. All types of reclaim which were tested vulcanized more rapidly than new rubber when the same proportion of S (based on rubber equivs.) was used. This rapid rate of vulcanization might have been due to (1) residual alkali; (2) unchanged accelerators still present; (3) depolymerization from heat and mastication; (4) a more advanced initial state of cure of the reclaim or (5) a curative action of oxidation products or of "polyprene sulfide." The expts. described were confined to the possible effects of (1), (3) and (4). Under carefully controlled conditions, it was found that small proportions of NaOH, such as are present in a mixt. contg. alkali reclaim, accelerated the rate of vulcanization but not to the same extent as did the reclaim, even when so little of the latter was added that the NaOH was in much smaller proportion. The absence of NaOH during devulcanization yielded a product which did not vulcanize so rapidly as a similar one prepd. with NaOH, but even the former vulcanized more rapidly than new rubber. Pale crepe which had been heated in water at different temps. for several hrs. vulcanized at about the same rate, regardless of the temp. of this preliminary treatment, from which it is judged that the high temps. used in devulcanizing are not responsible for the rate of vulcanization of the products. When reclaims were made from 2 mixts. which differed only in their original S content, the devulcanized products (which likewise differed in the combined S content) behaved in a similar way when tested in a mixt. contg. new rubber as well, so it is improbable that the proportion of combined S in a reclaim accounts for its rapid rate of vulcanization. On the other hand the higher the proportion of combined S in a reclaim, the poorer the aging of mixts. contg. the reclaim (cf. Boiry, *C. A.* **21**, 2574). In this connection expts. showed that even with NaOH present during devulcanization, the combined S increased considerably but that this could be partially prevented by preliminary heating with aq. NaOH at 60–65° to remove free S which otherwise reacted at high temps. even with NaOH present. Manufacturing problems arising from this rapid rate of vulcanization of reclaimed rubber are discussed.

C. C. Davis

Pigment reënforcement of reclaimed rubber. H. A. Winkelmann and E. G. Croakman. *Ind. Eng. Chem.* **20**, 134–7(1928).—The expts. deal with (1) the effect of different proportions of various types of pigments on the phys. properties of whole tire reclaimed rubber cured with S alone to different degrees; (2) the effect of activated accelerators on these pigmented reclaims and (3) the effect of varying the temp. of vulcanization. Only C black had a marked reënforcing effect when high proportions were added and the phys. quality continued to improve up to 20 vol. %, the max. tested. Thermatomic C, clays and Zn oxides had a slight effect, while whiting, barytes, blanc fixe and mineral rubber did not alter the phys. properties to any significant degree. This means that large quantities of whiting, barytes, etc., can be incorporated in such reclaimed rubber without impairing the phys. quality. With C black, clay or whiting present, the accelerators "Safex" and diphenylguanidine increased the rate of vulcanization and the former improved the phys. properties of the cured products. The effects on the phys. properties were judged by changes in the stress-strain curve, resistance to tear and to

abrasion and the plasticity. Better quality is obtained by curing reclaimed rubber at low temps. than at higher ones. C. C. DAVIS

Effect of high vs. low sulfur in vulcanizing reclaim. R. E. CARTLIDGE AND H. L. SNYDER. *Ind. Eng. Chem.* **20**, 137–40(1928).—An alkali tire reclaim was cured for different times at 142° with (1) 1.5–6.0% S and (2) in a tire-tread mixt. contg. 35% reclaim, 4% S on the new rubber and 1.5–5.0% on the rubber equiv. of the reclaim. The rubber equiv. of the latter was considered the difference between the integral reclaim and its acetone ext., ash, total S and C black. The results of the phys. tests are given in graphical form, besides which a table shows free and combined S, acetone and CHCl₃ ext. detns. In the particular mixt. contg. reclaim, the best quality and the longest optimum range of cure were obtained when 2–2.5% S (based on the whole reclaim) was used in conjunction with the 4% S for the new rubber. When the reclaim was cured with S alone, 3% (based on the whole reclaim) gave the best phys. quality. C. C. D.

A propos of "regenerated" rubber. A. D. LUTTRINGER. *Caoutchouc & gutta-percha* **24**, 13807–8(1927).—A discussion showing the fallacy of certain recent claims for regenerating rubber from waste products. **Correction.** *Ibid* **25**, 13844(1928).

C. C. DAVIS

The physical and mechanical properties of vulcanized rubber at high temperatures. II. A. VAN ROSSEM AND H. VAN DER MEIJDEN. *Kautschuk* 1927, 364–71; cf. *C. A.* **20**, 2431.—Further expts. deal with *changes in the stress-strain curve, in the hardness and in the plasticity of vulcanized rubber heated up to 147°.* Tests of different types of rubber carried out in the same way as in the earlier work proved that with a vulcanization coeff. of 3.0–3.2 the time necessary for rubber to become brittle at 147° varies greatly. Moreover rubbers which became brittle in the shortest time showed the poorest tensile strength at room temp. In illustration of this, the following data show the no. of min. at 147° for vulcanized rubber to become brittle and its max. tensile strength (kg. per sq. cm.): 1st latex sheet 1, 110; compo 1, 116; scrap crepe 2, 116; blanket crepe 5, 143; hard fine Para 30, 141; 1st latex crepe 30, 154; latex-sprayed rubber 15, 160. With samples which became brittle only after relatively long heating, the vulcanization coeff. increased during this heating and the vulcanization coeff. at which brittleness appeared was different in each case. When the samples which required 30 min. to become brittle with a coeff. of 3.2 were cured to a coeff. of 3.9, they then required only 2 min. to become brittle, so that brittleness appears in different rubbers at different coeffs. of vulcanization. The addn. of C black to the mixts. did not influence these relations. The *relation between the hardness of rubber and its coeff. of vulcanization* was detd. at room temp. and at 147°. Unexpectedly rubber with a low coeff. was harder at 20° than at 147° but with a high coeff. was harder at 147° than at 20°. This phenomenon was true of crepes, sheet, hard Para, compo and latex-sprayed rubber, the only differences being that the change occurred at slightly different coeffs. of vulcanization. The addn. of C black did not influence the phenomenon. Systematic tests in which the hardness of samples with different coeffs. was detd. at different temps. from 0° to 147° showed that around a coeff. of vulcanization of 4.8 the hardness was about the same over the entire temp. range, above and below 4.8 the changes being those described. The apparent discrepancy between the variation of the hardness of rubber with a high coeff. of vulcanization and its stress-strain curve at high temps. is explained by the fact that the stress at low elongations was greater at high temps. than at room temp. whereas the converse was true of the tensile strength. Therefore with a high coeff. of vulcanization the rubber was harder yet weaker at high temps. than at room temp. The plasticity detns. were made with a modification of the plastometer described by de Vries (*C. A.* **19**, 2281) on rubber with different coeffs. of vulcanization and at different temps., both the compression and the recovery being measured. The improvement over other methods lay in subjecting the rubber to const. pressure per unit area and measuring not only the decrease in thickness but also the immediate recovery and elastic after-effect on release. Only by obtaining this latter property at the same time is a true measure of plasticity obtained (cf. Bingham, *C. A.* **18**, 772). At 18° both the compression and the immediate recovery increased, while the elastic after-effect decreased with increase in the coeff. of vulcanization. The permanent deformation, *i. e.*, the plasticity, was negligible. At 100° undercured rubber showed partial recovery immediately and an elastic after-effect, and was plastic, whereas at longer cures the plasticity became negligible. The effects were similar at 130°, except for a greater elastic after-effect. At 147° the phenomena were very different. The immediate recovery increased with the coeff. of vulcanization, but much less than at lower temps. The permanent deformation due to plasticity was much greater and decreased with increase in the coeff. of vulcanization, ultimately becoming const. These results show that normally vulcanized rubber is plastic at 147°, whereas at 100–130° it is plastic only when undercured. Preliminary expts. showed that when cured rubber has a very low coeff. of vulcanization,

it can, like raw rubber, be racked and stabilized by cooling (cf. Feuchter, *C. A.* **21**, 1902).

C. C. DAVIS

Important reduction in the time of vulcanization of thin-walled dipped goods in sulfur chloride vapor. RUDOLF DITMAR AND GUSTAV BALOG. *Gummi-Ztg.* **42**, 858–9 (1928); cf. *C. A.* **21**, 1376.—When vulcanized in S_2Cl_2 vapor (1.5 cc. per 31.02 cc. vol.) from 0.5 to 45 min., films 0.03 mm. thick prepd. from pale crepe in C_6H_6 showed an alternating behavior. They were supple, elastic and aged well after cures of 4, 5 and 15 min., whereas they were distinctly overcured after cures of 3, 7–11 and 18–23 min. and after all cures above 30 min. The rhythmic phenomenon showed waves of increasing length and probably involved alternate aggregation and dispersion. When cured satisfactorily by this new rapid method, ZnO improved the aging greatly, lithopone, C black and TiO_2 gave good aging effects, whereas certain "Vulkan" colors impaired the aging. The aging tests involved exposure to strong sunlight. C. C. DAVIS

Is the vulcanization of rubber a balanced reaction? M. COMBET AND L. MILLET. *Rev. gén. mat. plastiques* **3**, 715–6(1927).—Properly cured rubber is defined as that in which the mech. properties (elongation, tensile strength, etc.) are an optimum and which has the longest life as regards the permanence of these mech. properties. From a discussion of the behavior of undercured, properly cured and overcured rubber when aged artificially at 87° in a Geer oven, the following theory of vulcanization is suggested. Natural rubber consists of 2 phases, α and β, which are in a state of equil., α being in a higher state of polymerization than β, which has the ordinary colloidal structure, and completely surrounds the latter. The relative proportions of the 2 phases differ according to the origin of the rubber. The reversible reaction $\alpha \rightleftharpoons \beta$ is possible and tends to go towards the right when the rubber ages, and simultaneously β tends to resinify. The aging of unvulcanized rubber is due to depolymerization of the α phase and its conversion into β; while the latter, being no longer protected, resinifies. On vulcanizing, the S first combines with the α phase, forming therewith a stable compd. and improving the mech. properties without affecting the initial flexibility of the rubber. In undercured rubber, *i. e.*, where sufficient total S has been added but which has not been sufficiently heated, on aging the reactions: $\alpha + S \longrightarrow \alpha S$ and also $\alpha \longrightarrow \beta$ take place, so that the combined S increases and at the same time the rubber has a tendency to become tacky. Properly cured rubber consists essentially of $\alpha S + \beta$, the latter phase being well protected and the former stabilized, with improvement in the mech. properties; the product has no tendency to tackiness, but hardens slightly on aging. In overcured rubber, all the α is converted to αS, and part or all of β to βS, which is much less stable than the former; hence the presence of free S irrespective of the proportion of S added to the mixt. The loss of elasticity is due to the combination of β with the S and there is further hardening on aging. Ebonite consists almost entirely of $\alpha S + \beta S$. Expts. carried out to prove this theory will be published later. A. P.-C.

Preparation of rubber cement. LESCUYER AND VILLENEUVE. *Caoutchouc & gutta-percha* **24**, 13732–3(1927).—A *mixer* is described and illustrated. C. C. DAVIS

New data on mineral rubber and its behavior with the ultra-accelerator "P-extra." RUDOLF DITMAR. *Gummi-Ztg.* **42**, 804(1928).—Eleven com. varieties of mineral rubber were tested in large proportion in a rubber mixt. accelerated by "P-extra." Some hardened the base mixt. much more than others, while none impaired the aging.

C. C. DAVIS

Synthetic rubbers. L. SLOIM. *Rev. gén. caoutchouc* 1927, No. 37, 3–6; cf. *C. A.* **22**, 510.—A discussion of the *chem. structure of rubber.* C. C. DAVIS

Patents

Rubber mixture. F. G. BREYER and C. W. FARBER. U. S. 1,649,782, Nov. 15. Dried co-pptd. ZnS and $BaSO_4$ impart to compounded rubber a resistance to abrasive wear greater than that given by "Special Grade Horsehead Brand" ZnO.

Roller apparatus for working rubber, etc. W. D. BARNET. U. S. 1,649,774, Nov. 15.

Rubber receptacles. A. FRASER. Brit. 266,041, Nov. 14, 1925. Tanks, battery boxes or other receptacles of rubber compns. are vulcanized under such conditions that a predetd. temp. gradient is maintained through the thickness of the article so that part of the article is vulcanized hard and the remainder is left soft and resilient.

Apparatus for vulcanizing tires or similar articles. L. A. LAURSEN. U. S. 1,650,-078, Nov. 22.

Vulcanizing rubber. J. TEPPEMA. Brit. 265,919, Feb. 12, 1926. For acceleration of vulcanization, there are used halogen derivs. of a mercaptothiazole, mercap-

toarylthiazole or mercaptobenzothiazole or their salts, *e. g.*, 6-chloro-2-mercaptoben-zothiazole, which may be prepd. by diazotizing 6-amino-2-mercaptobenzothiazole. The disulfides, or tolyl, naphthyl, anisyl or like thiazoles may be used. Cf. *C. A.* **21**, 3141, 4098.

Vulcanizing rubber. L. B. SEBRELL. Brit. 265,920, Feb. 12, 1926. As accelerators, there are used mercaptoarylthiazoles or their metallic salts, the substituted aryl structure of which contains "an element having an at. wt. greater than 13," *e. g.*, 6-nitro-2-mercaptobenzothiazole, prepd. by treating 2-mercaptobenzothiazole with concd. HNO$_3$, or halogenated, sulfonated or hydroxy derivs. or amino compds. Cf. *C. A.* **21**, 3768.

Vulcanizing rubber. W. B. BURNETT and I. WILLIAMS. Brit. 265,930, Feb. 12, 1926. For accelerating vulcanization, there is used a condensation product of 1 mol. of a primary amine such as aniline, butylamine or *o*-tolyl guanide and 2 or more mols. of an *α*, *β*-satd. aldehyde such as butyraldehyde, heptaldehyde or propionaldehyde. Weak org. acids are preferred as condensing agents but various other specified condensing agents also may be used. These accelerators are well adapted for use in vulcanizing rubber compns. contg. gas black and are operative at temps. above 100° only. Brit. 265,931 specifies carrying out processes such as described in Brit. 263,853 (*C. A.* **22**, 186) for the production of aldehyde amine condensation products suitable for use as accelerators in the presence of an acid or substance of acid reaction such as HOAc, propionic acid, butyric acid, stearic, oleic, salicylic, or picric acids, HCl, H$_3$PO$_4$, H$_2$SO$_4$, ZnCl$_2$, amine salts, acid anhydrides or halides. Several examples are given.

Composition for sealing leaks in tires. F. W. FISCHER and G. F. DALLAS. U. S. 1,650,867, Nov. 29. A semi-liquid mixt. is formed of flaxseed meal and uncured rubber gum softened with linseed oil.

Composition for sealing punctures in tires. T. VAN BOECKHOUT. Brit. 266,374, Feb. 19, 1926. H$_2$O 50, dextrin 8, plumbago 35 and "plaster" 1.5 parts.

Vulcanizing latex. P. SCHIDROWITZ and VULTEX, LTD. Brit. 266,418, Oct. 28, 1925. Direct vulcanization as described in Brit. 193,451 (*C. A.* **17**, 3430) is applied to a concd. latex, preferably contg. at least 53% of rubber, to produce a spreadable, reversible, uncoagulated, vulcanized mass.

Vulcanizing rubber. C. W. BEDFORD. U. S. 1,650,975, Nov. 29. An addn. product of a metallic salt such as ZnSO$_4$ or HgCl$_2$ and a primary org. amine such as *p*-aminodimethylaniline or aniline is used as an accelerator in vulcanizing with S or similar vulcanizing agents. Cf. *C. A.* **21**, 674, 4098.

Compounding rubber. H. A. ENDRES. U. S. 1,652,141, Dec. 6. An excess of BaCl$_2$ is admixed with Na$_2$SO$_4$ and latex is added to the mixt. and coagulation of the rubber in the latex is effected.

Compounding and vulcanizing rubber. O. H. SMITH. U. S. 1,651,737, Dec. 6. The surface of a sheet or piece of rubber is treated with a mixt. of ZnO or other metal oxide, S and an org. accelerator such as dibenzylamine and hydroxybutyl thiocarbonic acid disulfide and the material is then heated to effect vulcanization.

Concentrating latex and similar materials. W. A. GIBBONS and M. G. SHEPARD. U. S. 1,651,764, Dec. 6. A heated gas is passed over the surface of the material and the formation of a film on the surface is continuously checked during the evapn. of moisture, *e. g.*, by the action of a stirring device. NH$_3$ may be added. An app. is described.

Heat-exchange roll adapted for working rubber. F. H. BANBURY. U. S. 1,651,502, Dec. 6.

Uniting layers of rubber to rubber or to other materials. F. J. DAVIS. U. S. 1,654,240, Dec. 27. The contact face of a layer of rubber is treated with a soln. of rubber, rubber latex is then sprayed on the treated surface, moisture is evapd. from the latex applied, to form a thin film of rubber over the layer of rubber in soln. and the layer of material thus prepd. is suitable for attachment to leather.

Uniting and repairing rubber sheets and other rubber articles. H. A. BLOCKER and M. L. MULLIN. U. S. 1,652,926, Dec. 13. A rubber soln. contg. rubber 5 and naphtha 95% is mixed with a larger quantity of a mixt. of equal proportions of ether and C$_6$H$_6$.

Rubber mold. A. P. TALLMAN. U. S. 1,652,218, Dec. 13. The surfaces of molds suitable for molding rubber are coated with a baked japan with which is incorporated a rubber lubricating material such as Al stearate.

Porous ebonite articles. M. WILDERMAN. U. S. 1,651,567, Dec. 6. In forming diaphragms, filters or other articles, partially cured ebonite powder, shavings or the like is compressed sufficiently to form a porous mass of connected particles which are vulcanized together.

Fabrics for use in vulcanization of rubber. S. M. CADWELL. U. S. 1,651,751, Dec. 6. Fabrics formed of vegetable fiber and used in connection with vulcanization

of rubber and rendered more durable by treating them with a reagent such as hydrated Na phosphates are adapted to neutralize acids developed during the vulcanization.

Vulcanizing rubber. H. GÜNZLER and W. ZIESER. U. S. 1,653,502, Dec. 20. The amide of formic acid is used as an accelerator.

Vulcanizing rubber. S. J. PEACHEY and A. SKIPSEY. U. S. 1,653,821, Dec. 27. Rubber is treated with a sulfide of P and then with NH_3.

Vulcanizing rubber. W. A. GIBBONS. U. S. 1,654,167, Dec. 27. Drying and vulcanizing of substantially uncoagulated latex is effected in the presence of Zn dimethyldithiocarbamate or other org. accelerator capable of causing vulcanization at temps. (such as 100°) substantially below those ordinarily employed for vulcanization.

Vulcanizing rubber. SOC. ITALIANA PIRELLI. Brit. 266,732, Feb. 24, 1926. Salts of K or Rb are used as accelerators, e. g., the acetate, butyrate, valerate, palmitate, stearate, phenylacetate, benzoate or succinate.

Vulcanizing rubber with sulfur. C. O. NORTH. U. S. 1,651,931, Dec. 6. A mixt. of accelerators is used, including the aldehyde deriv. of dehydrated ethylidene aniline and the aldehyde reaction product of the aldehyde deriv. of dehydrated ethylidene aniline. Cf. *C. A.* **21**, 3000.

Vulcanizing rubber. H. W. ELLEY. U. S. 1,652,101, Dec. 6. Vulcanization is accelerated by the use of combined Zn and methylene dimethyl thiuram disulfide or a similar compd.

Apparatus for stretch-testing of rubber. R. P. STEVENSON. U. S. 1,656,246, Jan. 17.

Manufacture of porous or spongy rubber articles. HELSINGBORGS GUMMIFABRIKS AKTIEBOLAG. Swed. 63,718, Sept. 13, 1927. The rubber is mixed with polymerized aldehydes which are solid at normal temp. At the vulcanization temp. these substances are depolymerized with formation of gases or liquids with high vapor pressures.

Reclaiming rubber. G. J. MILLER. U. S. 1,657,171, Jan. 24. Comminuted rubber material contg. cotton is boiled in an acid soln. such as $ZnCl_2$ and HCl which will dissolve the cotton and some of the acid-sol. fillers, the remaining rubber compd. is sepd. from the soln. and washed, placed in kerosene and heated to 120–150° to remove impurities so far as possible from the rubber without dissolving the latter; the kerosene and rubber are sepd. and the rubber is washed with a suitable volatile washing liquid such as gasoline, CS_2 or CCl_4 to remove the kerosene and is then dried. Cf. *C. A.* **21**, 3490.

"Regenerating" rubber. C. DANIER. U. S. 1,656,694, Jan. 17. Rubber such as old tire casings is impregnated with an unpolymerized rubber distillate and then treated with a mineral acid such as HCl to polymerize the distillate.

Vulcanizing rubber. W. SCOTT. U. S. 1,656,834, Jan. 17. Vulcanization with S is effected in the presence of an accelerator comprising a crotonaldehyde deriv. of the reaction product of di-o-tolylguanidine and mercaptobenzothiazole or other aldehyde deriv. of the reaction product of an org. base and a mercapto compd. contg. a C-SH group. Cf. *C. A.* **21**, 3284.

Vulcanizing rubber. M. L. WEISS. U. S. 1,657,522, Jan. 31. Vulcanization is accelerated by use of reaction products of diphenylguanidine with 2,6-dimercapto-3,5-diphenyl-4-ketothiopyran or similar substances. Cf. *C. A.* **21**, 1031.

Rubber vulcanization accelerator. W. SCOTT. U. S. 1,656,891, Jan. 17. An accelerator is prepd. by reacting with an aldehyde such as crotonaldehyde upon the reaction product of an org. base such as di-o-tolylguanidine and a mercapto compd. contg. the group C-SH, e. g., mercaptobenzothiazole. Cf. *C. A.* **21**, 196, 3490.

Apparatus for vulcanizing rubber articles. R. W. SNYDER. U. S. 1,656,874, Jan. 17.

Oven for vulcanizing rubber articles. H. R. TILL. U. S. 1,656,251, Jan. 17.

Apparatus for vulcanizing inner tire tubes. C. H. ROTH. U. S. 1,656,870, Jan. 17.

Composition for sealing tire punctures. B. G. HARRINGTON. U. S. 1,657,081, Jan. 24. A dehydrated mixt. is prepd. contg. finely divided SiO_2 and Al_2O_3 together with smaller proportions of mica and soapstone, in fine powd. form.

Apparatus for marking rubberized fabrics. P. S. SHOAFF. U. S. 1,656,872, Jan. 17.

Playing ball of rubber composition. G. H. WILLIS. U. S. 1,656,462, Jan. 17. Cores of golf balls or similar playing balls are formed of a homogeneous elastic mass of animal hair and rubber.

Rubber composition for expansion joints of concrete roads, etc. E. B. COWEN. U. S. 1,654,793, Jan. 3. Rubber is mixed with cotton fiber, high-test asphalt and a filler or wear-resisting substance such as clay or lime.

Removal metal cores from hollow rubber articles after vulcanization. C. D. BLACK. U. S. 1,656,312, Jan. 17. An elec. induction heater is used, supplied with a. c. of a frequency of about 10,000–20,000 cycles per sec.

Bonding leather or other surfaces with rubber compositions. E. HOPKINSON. U. S. 1,657,472, Jan. 31. Each of the surfaces to be joined is coated with latex, the latter is allowed to dry, and the dried surfaces are coated with rubber cement and then united. Cf. *C. A.* **21,** 1031.

Hydrocyclocaoutchouc. H. STAUDINGER. U. S. 1,654,844, Jan. 3. See Brit. 263,862 (*C. A.* **22,** 186).

Substitute for catgut. A. E. PENFOLD, R. TRUESDALE and R. C. SMITH. U. S. 1,654,944, Jan. 3. Strands of silk, cotton or similar material are impregnated with a soln. contg. a relatively large proportion of deresinated gutta-percha and a relatively small proportion of S; the strands are twisted together, pressed, vulcanized and superficially finished to adapt them for use on musical instruments, tennis rackets, etc. The soln. used may comprise deresinated gutta-percha 15–23 and S 1.5% with a solvent such as toluene.

Conversion of Rubber into Thermoplastic Products with Properties Similar to Gutta-Percha, Balata, and Shellac[1]

I—Methods of Preparation and General Properties

By Harry L. Fisher[2]

THE B. F. GOODRICH CO., AKRON, OHIO

By heating in sheet form a mixture of rubber with
approximately 10 per cent of its weight of either an or-
ganic sulfonyl chloride or an organic sulfonic acid, for
several hours at 125–35° C., the rubber is converted
into tough, thermoplastic products resembling gutta-
percha and hard balata. If heated similarly in bulk
there is a pronounced exothermic reaction and the
products formed are hard and thermoplastic like shel-
lac. p-Toluenesulfonyl chloride and p-toluenesulfonic
acid are suitable reagents. A mixture of 7.5 parts of
p-phenolsulfonic acid and 100 parts of rubber, under
similar conditions, gives a flexible product similar to
gutta-percha, which is soluble in benzene, is a very good
adhesive, and is the basis of the Vulcalock process.
Five parts of concentrated sulfuric acid milled into 100

parts of rubber and heated as above give balata types
but not the soluble shellac types.

The products have been given the general name
"thermoprene," and the following suffixes are used in
order to designate the different types: GP, HB, and SL.

THE hydrocarbon of gutta-percha has long been known
to have the same empirical formula as that of the rub-
ber hydrocarbon—namely, C_5H_8—and also the same
unsaturation—one double bond for each C_5H_8 group.[3] The
same is true of the balata hydrocarbon although the experi-
mental data in this case are meager.[4] The physical prop-
erties, however, are quite different, gutta-percha and balata
being thermoplastics. Many attempts have been made to
convert the more abundant rubber hydrocarbon into the less
abundant, though very valuable, gutta-percha and balata
hydrocarbons, but none have been successful. Harries[5] de-
scribes his attempt in which he used sulfuric acid on rubber
in solution, but the product was amorphous and friable. He
could not obtain it ash-free, stating: "I think, however, that
it has the same composition, $C_{10}H_{16}$, as rubber, but probably
a higher molecular weight." That such a conversion is
probable is indicated by the recent work of Staudinger,[4] who
has shown that the three corresponding hydrogenated hy-
drocarbons are identical as judged by their refractive indices
and composition. The present writer has not succeeded in
making this complete change, but he has been able to convert
rubber into isomeric hydrocarbons which are similar not only
to gutta-percha and balata but also to shellac.[6]

Preparation

Concentrated sulfuric acid reacts rapidly with rubber in
solution, precipitating and transforming it into a much less
unsaturated, insoluble, high-melting substance.[6,7] In study-
ing the action of sulfuric and various other acids on rubber
in solution, the writer noted that chlorosulfonic acid (HO-
SO_2Cl) seemed to work even more rapidly than sulfuric acid.
Thinking that this difference was due to the replacement of
one OH-group with Cl, he tried to mitigate its action by using
a derivative in which the other OH-group was replaced with
an organic radical. p-Toluenesulfonyl chloride was chosen
and, since it is a solid, it was milled directly into the rubber.
A chemical double decomposition was expected because the
reagent was no longer an acid, but stoichiometric quantities

[3] Caspari, *J. Soc. Chem. Ind.*, **24**, 1274 (1905); Harries, "Untersuch-
ungen über die natürlichen und künstlichen Kautschukarten," p. 119 (1919).
[4] Harries, *op. cit.*, p. 124; Staudinger, *Kautschuk*, p. 8 (September,
1925).
[5] *Op. cit.*, p. 6.
[6] U. S. Patent 1,605,180 (1926); Canadian Patent 256,567 (1925).
[7] Kirchhof, *Kautschuk*, p. 1 (January, 1926). The product is generally
partially oxidized. Compare also Marquis and Heim, *Bull. soc. chim.*, **13**,
862 (1913).

could not be used under the conditions employed, only 40
parts instead of the theoretical equivalent, 280, on 100 of
rubber being milled into the rubber on the first trial. Fifty
grams of rubber were used. A sample of the soft mixture was
heated on a watch glass in an air oven for 1 hour (10 to 15
minutes would have been sufficient) at 105° C., and a black,
shiny mass was obtained which while hot yielded to the pres-
sure of the thumb nail and was not soft and sticky like most
heated rubber batches. Upon cooling it set to a hard, brittle
mass! The original rubber mix was then milled with enough
rubber to reduce the proportion to 20 of the reagent to 100 of
rubber and a sample heated again for the same period. There
were evidences of stiffening at the end of the hour, and
after having been heated in the oven overnight it became hard
and very tough, although its upper surface consisted of a film
of resilient rubber. This rubbery film was soon found to be
characteristic, since some of the reagent distils out and it was
learned that small amounts of the reagent—5 parts[3] per 100 of
rubber—give a resilient product which is rubbery but "short"
and non-thermoplastic. Gravity disks ($1^7/_8$ inches in di-
ameter and $^3/_{16}$ inch thick, of the type ordinarily used for
determining the specific gravity of commercial stocks) of the
mix with 20 parts cured for 30 and 60 minutes at 141° C. came
out black, rather hard, and so tough that they could not be
broken with the fingers. They cut like a hardened balata,
softened in hot water, and could then be molded. Thus was
opened up a new field of thermoplastics with properties that
could be varied at will from hard, brittle types resembling
shellac to rather soft, very tough types resembling gutta-
percha and balata.

The soft balata types and the hard shellac-like products
can be made from a mix containing as low as 10 parts of the
reagent, depending on the method of heating. At tempera-
tures around 125–45° C., in a thin sheet mold in a press, or in
comparatively thin sheets in an air oven, the gutta-percha
and balata types are formed. After 30 minutes' heating
at 141° C. they are rubbery and resilient, in 2 hours they are
balata-like inside, and in 12 hours they are hard and tough.
When in bulk, however, the shellac type is formed almost
entirely. It is an interesting fact, also known in ordinary
vulcanization with sulfur, that during the "cure" an exo-
thermic reaction takes place with consequent rise in tempera-
ture. In thin sheets this heat is readily dissipated, but in
bulk, on account of the slow rate of heat conductance, the
heat accumulates, and the internal temperature often reaches
225° C., even in comparatively small batches. A sample
of the mix in a test tube quickly heated in a metal bath
to the same high temperature is converted into the shellac
type within a few minutes, but larger batches at the lower
temperatures require several hours. The time when this

[3] Parts as used throughout this paper will always mean "parts per 100
of rubber."

exothermic reaction shows itself is quite characteristic, depending upon the concentration of the reagent, the bulk of the batch, and the temperature of the surrounding medium. For 500 grams of a batch of 10 parts heated in an oven at 135° C. this exothermic reaction becomes decidedly noticeable at 180 minutes, and for a batch of 20 parts in about half this time. A 100-part batch reacts violently even while on the mill. Also in a press, if the bulk is fairly large—for example, 2 inches thick—a goodly portion of the batch is converted into the shellac type. Gases are always formed, consisting of sulfur dioxide, hydrogen sulfide, and others of a peculiar, characteristic odor. In the larger batches, on account of the high temperature, the shellac type of material becomes very limpid during the reaction and the gases bubble out easily, leaving a fine solid product, which when cold breaks with a typical conchoidal fracture. The balata-like batches are stiffer even while hot and therefore the gases do not all escape and a honeycomb mass results. However, such a product can be milled and homogenized on a hot mill and thus be freed from bubbles.

Other organic sulfonyl chlorides react similarly such as benzene-, β-naphthalene-, m-nitrobenzene-sulfonyl chloride. Liquid reagents like benzenesulfonyl chloride can advantageously be added to a solution of rubber, the solvent evaporated, and the residual mix heated as usual, or, better still, the rubber is allowed to soak up the reagent for several hours in a sealed tube or autoclave and then heated. Aliphatic sulfonyl chlorides also can be used, butanesulfonyl chloride giving a satisfactory reaction. Basic nitrogen groups more or less neutralize the action of the sulfonyl chloride group. For example, acetanilide-p-sulfonyl chloride gives only a partial reaction. The simple sulfonyl chlorides dissolve in the rubber and sometimes form almost transparent sheets on the mill. Then, on cooling and standing the crystals "bloom" out on the surface just as sulfur does.

Organic Sulfonic Acids

At first it was thought that the organic sulfonyl chlorides reacted with the rubber hydrocarbon, giving off hydrogen chloride and forming sulfones, partially represented as follows: $CH_3C_6H_4.SO_2.C_5H_7$. Accordingly, there seemed to be no reason why the corresponding sulfonic acids should not react, forming similar sulfones and giving off water instead of hydrogen chloride. p-Toluenesulfonic acid was therefore milled into rubber and products apparently identical with those formed with the sulfonyl chlorides were obtained. These sulfonic acids can be milled into rubber readily and of course do not give off the sharp vapors of the sulfonyl chlorides, although some sulfur dioxide and the peculiar characteristic odor are given off. Furthermore, since they are non-volatile the reaction products are more homogeneous, there being no rubbery film on the outside of batches. These

acids do not dissolve appreciably, if at all, in the rubber; nevertheless the same reaction types of products are formed under similar conditions of concentration, time, temperature, and conditions of heating. In other words, resilient, rubbery products, soft gutta-percha and hard balata types, and shellac-like products are obtained with the use of the sulfonic acids as with the sulfonyl chlorides. It is difficult to obtain the sulfonic acids anhydrous and also free from sulfuric acid, but a little water makes no special difference, and the sulfuric acid, although not necessary for the reaction, helps to give products which are tougher and less brittle than those obtained when the pure sulfonic acid is used alone. Sulfuric acid also raises the softening temperature.

As a rule when there is enough reagent present to bring about the characteristic exothermic reaction, the product formed is hard and shellac-like. But when 7.5 parts of p-phenolsulfonic acid are used and the batch is heated in the oven as usual, about 6 hours at 141° C., the same exothermic reaction takes place, but the result is a brown, flexible product, which is tough, millable on a cold mill, and resembles gutta-percha in many of its properties.

Early in the work it was noticed that the products showed a strong tendency to adhere tenaciously to metals, especially iron, and later the product just described was found to be unusually good as an adhesive and, in particular, for making rubber stick to iron, wood, etc. It became the basis of the Vulcalock process.[9]

Batches of 10 parts of p-phenolsulfonic acid and rubber, heated in bulk, give hard and tough shellac-like products, whereas when heated as $1/r$-inch sheets in soapstone for 48 hours at 110° C. they give the balata type.

A mix of 15 parts of m-nitrobenzenesulfonic acid, heated in bulk for 4 hours at 150° C., also gives a somewhat flexible shellac-like product; a mix of 10 parts gives a hard balata-like product, and a mix of 20 parts "cures up" and "breaks" on the mill.

Generally, organic sulfonic acids containing a free sulfonic group act chiefly like p-toluenesulfonic acid. Such, for example, are benzene-, β-naphthalene-, 2,5-dichlorobenzene-, 2-chlorotoluene-, 4-nitrochlorobenzene-2-sulfonic acid, benzene-disulfonic acid, sulfosalicylic acid, 1-naphthol-4-sulfonic acid, phenoldisulfonic acid, pyrogallolsulfonic acid, etc. Substances containing potential free sulfonic groups, such as o-sulfobenzoic anhydride, react similarly, but those in which the sulfonic group is more or less intramolecularly neutralized, as in sulfanilic acid, either do not react at all or only show slight activity. Of all the sulfonic acids containing basic nitrogen groups tried, including naphthionic, metanilic, sulfanilic, o-nitraniline-p-sulfonic, p-phenetidinesulfonic, β-naphthylaminedisulfonic, 8-hydroxyquinoline-5-sulfonic, 2,4-dihydroxyazobenzenesulfonic acid, etc., only one, 2-naphthyl-

[9] Geer, Canadian Patent 256,797 (1925).

amine-1-sulfonic acid, showed any marked signs of a good reaction and that reaction was only about half complete. The inorganic aminosulfonic acid ($NH_2.SO_2.OH$), even in a mix of 40 parts, gave only a resilient mass.

Aliphatic derivatives such as ethylsulfonic acid and kerosene sulfonic acid react regularly.

Syntans, both the soluble and insoluble reaction products of p-phenolsulfonic acid and formaldehyde, give the usual hard thermoplastic products, and Twitchell's reagent. represented by cymenesulfostearic acid, gives a soft, somewhat thermoplastic product.

These products formed with the sulfonic acids, wherever tested, are only a little more than half as unsaturated chemically as the original hydrocarbon.

Sulfuric Acid

Every one brought up in a rubber factory learns very definitely one important rule—not to have a trace of any inorganic acid in a rubber mix;[10] and the writer was no exception. It therefore took some little time to break down such a psychological barrier and think of mixing sulfuric acid into rubber! Yet there seemed to be no reason why sulfuric acid should not act something like p-toluenesulfonic acid. Fossil flour was chosen as a carrier for the acid, and in the first experiment 5.50 grams of concentrated sulfuric acid and 2.75 grams of fossil flour were mixed into 50 grams of pale crepe on a small mill. The rubber turned red-brown, became sticky, went over on the back roll, gave off the odor of sulfur dioxide, and then suddenly stiffened and became so hard and tough that it could only be removed by means of a chisel. A mixture of 5 parts worked all right and on being heated in the oven for 3 hours at 138° C. became a hard, very tough, thermoplastic mass. In larger batches it was very difficult to complete the mixing, since a partial reaction makes the rubber tough and "short," and causes it to drop off the mill. This difficulty was overcome, however, by using diluted acid of 70 to 80 per cent concentration. Furthermore, by keeping the rubber thin on the rolls and thereby keeping down the temperature, even concentrated sulfuric acid without any carrier or without being diluted was milled in! On corrugated rolls acid to the extent of 33 parts, mixed with clay, has been milled in. These high-acid batches crumble off the mill, but some even then can be molded in a plunger mold.

The sulfuric acid batches cure up to thermoplastic, hard balata types. The temperature rise is considerable in bulk and yet none of these batches has ever been observed to go over into the shellac type of product. The reason for this

[10] Goodyear, "Gum Elastic," Vol. I, p. 154 (1855); Whitby, *India Rubber J.*, **68**, 618 (1924), states: "The fact * * * that the material extractable from raw rubber by means of acetone consists largely of free acids is not without an ironical aspect, when it is recalled that the presence of any acidic material in rubber has generally been regarded with suspicion, and has often been roundly and indiscriminately declared to be harmful."

is not clear. On being heated in thin sheets they can be made to become more or less brittle, depending upon the usual factors of concentration, time, and temperature. Those containing water must, of course, be heated longer than those without it. Batches of 5 parts in a sheet mold in a press give gutta-percha-like products in 3 hours at 177° C., and hard balata types in 6 hours. In bulk or in large sheets it is usually best to heat for 24 hours or longer at 110–25° C. The weight loss is in most cases, not counting any water, approximately 4 per cent. Batches of 3 parts give soft, resilient masses resembling "short," soft-vulcanized rubber, which mill very much like cured inner-tube scrap. The sulfuric acid batches while being heated give off an odor reminiscent of chicory.

In attempting to carry the sulfuric acid into the rubber in the form of an organic combination, diphenylamine sulfate was tried and found to work very well. Only salts of similar very weak bases will react. Other amine sulfates such as those of aniline, benzidine, 2,4-dimethylquinoline, and guanylurea, and also of ammonia, show no apparent action. Crystalline aluminum sulfate and ferric sulfate show a partial reaction, probably on account of the acid formed by hydrolysis. Cellulose (cotton) (4 parts) dissolved in concentrated sulfuric acid (10 parts) gives the usual reaction. Only 2 parts of sulfuric acid with 10 parts of trioxymethylene in 100 parts of rubber, when heated as usual, give a semihard rubber sponge. Dimethyl sulfate reacts like sulfuric acid.

General Notes and Observations

OTHER RUBBERS—Pale-crepe rubber was used in most of the work, but other types of raw rubber can also be used. The relative proportions of the reagents, the time, and the temperature generally have to be varied according to the rubber or its physical condition. Furthermore, the products will vary under similar treatment according to the physical condition of the original rubbers. Synthetic rubbers, such as the German methyl-rubber-W and methyl-rubber-H, undergo similar transformations, physically and chemically. Reclaimed rubbers also react, but larger proportions of reagents must be used since reclaims generally contain alkaline substances which neutralize the reagents. Products with much better properties can be obtained with reclaimed rubbers if some pale crepe is added. The organic sulfonyl chlorides react the best with reclaims.

MILL ROLLS—The reagents apparently cause no damage to the steel mill rolls, for rolls that have been used for several years have shown no noticeable deterioration. It is, of course, advisable to clean off any film of acid that may remain at the end of a day's work by means of an old piece of rubber.

WORKING AND COMPOUNDING THE PRODUCTS—Since the products are thermoplastics they can be milled on hot rolls.

The shellac-like products work very much like shellac itself but have more "body" while hot. The gutta-percha- and balata-like products sometimes mill very nicely, and sometimes they are "short" and tend to "break." Usually by keeping the rolls tight even this difficulty can be overcome. The phenolsulfonic acid product (7.5 parts) can be milled on cold rolls. Compounding is done in the usual manner on the hot rolls, and alkaline ingredients can be included, if desired, in order to neutralize any acid.

Vulcanization

The products can be vulcanized by heating with sulfur, but since they are chemically less unsaturated than rubber they do not take up so much sulfur. Sulfur converts them into non-thermoplastics if the heating is long enough. In fact, even 2 parts of sulfur with long heating (about 15 hours at 141° C.) converts them into insoluble, non-thermoplastic products like hard rubber. If sulfur is milled into the original mixture along with the acid the product will be much higher softening, and if more than about 20 parts of sulfur is used the product will scarcely soften within the thermoplastic range. The action of sulfur will be discussed further in the second part of this paper.

Solubility

The solubility depends on the type of product. The gutta-percha-like product from 7.5 parts of p-phenolsulfonic acid can be made completely soluble in the ordinary rubber solvents, such as benzene, chloroform, carbon tetrachloride, carbon bisulfide, gasoline, turpentine, tetralin, etc. The shellac type dissolves almost completely in these same solvents, depending on how it is made and the amount of sulfuric acid used in the mixture. These solutions are much less viscous than solutions with corresponding amounts of ordinary, masticated rubber. Concentrations of 25 per cent are easily obtained. The other types are more or less soluble, but those made with sulfuric acid alone are some- times very difficultly soluble, especially if they have had a long heating. Vulcanization with sulfur makes them all much less soluble.

General Chemical and Physical Properties

The general chemical properties are very much the same as those of the rubber from which they are derived, except that, as already mentioned, they are less unsaturated. They form addition products with hydrogen chloride, sulfur, oxygen, etc. Bromine substitutes as well as adds. They are re- sistant to the action of alkalies and inorganic acids, except nitric acid, especially when these are dilute. The chemical properties will be discussed in greater detail in Part II of this paper.

The general physical properties have already been de- scribed. In addition, they absorb only a very small amount

of water. Furthermore, the gutta-percha- and balata-like products lack the snap of the natural varieties. When freshly prepared and molded they all have a so-called surface tack, noticeable as a rule only when the fingers are warm and moist with perspiration.

A more definite idea of the physical properties of some of the products can be obtained from the accompanying table. The samples were generally homogenized on a hot mill and then molded as 6 by 8 by $^1/_4$-inch sheets or as disks $^1/_4$ inch in thickness and 7 inches in diameter.

Physical Properties of Products

Tests[a]	A	B	C	D	E	F
Specific gravity (room temperature)	0.980	0.999	1.016	0.993	0.993	1.003
Tensile strength, lbs. per sq. in. (22° C.)	2600	2300	4800	4700	660	Too brittle to test
Elongation at break, per cent	27	29.8	1.3	1.7	0.6	
Impact strength, in. lbs. per sq. in. at 0° C.	50	20.8	41	42	6.6	1.4
Ultimate compressive strength, lbs. per sq. in.	5400 (21° C.)	3850	10,600 (24° C.)	8600 (32° C.)	9000 (32° C.)	7100 (26° C.)
Ultimate transverse strength, lbs. per sq. in. (21° C.)[b]	8100	4800	7200	7000	2140	1600
Cold flow, per cent (50,000 lbs. load)	38.6 (21° C.)	38.2	17.3 (24° C.)	30.4 (24° C.)	34.3 (24° C.)	22.8 (24° C.)
Dielectric strength, volts per mm.	47,500	36,500	50,000	55,200	51,800	53,200
Thickness of sheet, mm.	(0.91)		(0.94)	(1.07)	(0.76)	(0.89)
Softening temperature, ° C.	Room temperature	...	65	77	..	..

[a] The author is indebted to E. O. Dieterich for the determinations of these physical constants.
[b] Loaded to failure rapidly.

A—A gutta-percha type prepared from 100 parts of pale crepe and 7.5 parts of *p*-phenolsulfonic acid by heating 1075 grams in a 1-gallon can for 6 hours at 141° C.

B—A hard balata type prepared from 100 parts of pale crepe and 10 parts of *p*-toluenesulfonyl chloride by heating $^1/_2$-inch sheets in a tray for 8 hours at 100–5° C. and then 8 hours at 110–5° C.

C—A hard balata type prepared from 100 parts of pale crepe, 4 parts of concentrated sulfuric acid, and 2 parts of fossil flour, by heating in bulk for 24 hours at 120–5° C. in an oven.

D—A very hard balata type prepared from 100 parts of pale crepe and 10 parts of a moist crystalline mixture consisting of approximately 63 per cent *p*-toluenesulfonic acid, 12 per cent sulfuric acid, and 25 per cent water by heating $^1/_2$-inch sheets in soapstone for 30 hours at 110° C. and then 67 hours at 115–25° C.

E—A shellac type prepared from the same batch as *D* but heated in bulk for approximately 4 hours at 125° C. (Note the effect of the sulfuric acid as compared with *F*.)

F—Also a shellac type but prepared from 100 parts of pale crepe and 12.5 parts of β-naphthalenesulfonic acid, and heated in bulk in an oven for several hours at 145° C.

Nomenclature

Ostromislenski,[11] Kirchhof,[7] and Staudinger[12] have also noted the diminution in the chemical unsaturation of the products formed from synthetic and natural rubber in solution under the influence of acidic reagents,[13] such as zinc bromide, sulfuric acid, zinc chloride, respectively, and very properly designated the change as due to cyclic formation. The products described in this paper, according to their unsaturation, do not fall directly into the monocylic or polycyclic nomenclature, and furthermore their properties vary much more. Therefore, it has seemed best to give these new derivatives names which are descriptive and also indicative of their origin. The general name chosen to represent them is "thermoprene," signifying a thermoplastic, unsaturated hydrocarbon derived from polyprene, Weber's name for the rubber hydrocarbon. In order to differentiate between the varieties it is suggested that to the general name certain letters be added to signify the type, such as GP for gutta-percha, HB for hard balata, and SL for shellac-like—for example, thermoprene-GP, thermoprene-HB, and thermoprene-SL.

Industrial Applications

The products can be used in various operations where thermoplastics are ordinarily employed; for molded articles, particularly molded electrical and cable insulation, diaphragms, phonograph records, etc.; and for paints and adhesives, especially for causing rubber to adhere to metal and wood in connection with tank linings, chutes, ball mills, etc.

Acknowledgment

[11] *J. Russ. Phys. Chem. Soc.*, **47**, 1915 (1915); *C. A.*, **10**, 1947 (1916).
[12] *Helv. Chim. Acta*, **9**, 529 (1926).
[13] Although Ostromislenski did not mention it, there appears to be no doubt that the transformation he described was due to the presence of the zinc bromide formed during the reaction.

II—Chemistry of the Reaction

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**The shellac-like products formed by the action of
organic sulfonic acids on rubber have been studied
chiefly. After purification the chief constituent is
found to be a hydrocarbon with the same empirical
formula as that of rubber, C_5H_8, and it is 55 to 60 per
cent as unsaturated as the rubber hydrocarbon. Addi-
tion products of hydrogen chloride and hydrogen bro-
mide have been prepared. Vulcanization with sulfur
gives a maximum combined-sulfur content of about 21
per cent, corresponding to 57 per cent unsaturation as
compared with rubber. Oxidation, hydrogenation,
bromination, nitration, etc., have also been studied.
The purified hydrocarbon is white and is completely
soluble in the rubber solvents and insoluble in alcohol,
acetone, etc. It is much more stable toward heat than
rubber. The gutta-percha and balata types are only
partially soluble, but analyses, yields, etc., indicate
that they consist of similar isomeric hydrocarbons.**

WHEN organic sulfonyl chlorides are milled into
rubber and the mixtures are heated, the rubber is
converted into thermoplastic products which, accord-
ing to the conditions employed, resemble gutta-percha, bal-
ata, or shellac. As mentioned in Part I, it was thought at
first that the reagent reacted with the rubber hydrocarbon
possibly forming sulfones; otherwise the reaction seemed very
much like ordinary vulcanization since the results varied
with the time and temperature and concentration of the
reagent, and since even the amounts of the reagent used were
comparable with those of sulfur. In fact, when compared
with the customary 5 parts of sulfur (32) on 100 parts of
rubber, 10 parts of p-toluenesulfonyl chloride (190.5) is
only one-third the molecular equivalent. The idea of sul-
fone formation led to the use of the organic sulfonic acids,
which gave even more useful products, and finally to the
use of ordinary sulfuric acid itself. This theory, however,
was proved to be untenable.

After a rather thorough study of the different types of
reagents and the conditions under which the various prod-
ucts are formed, a detailed study of the chemistry of the
reaction was undertaken. The jet black, shellac-like prod-
ucts (thermoprene-SL) were examined first, since they
are almost completely soluble in benzene, carbon tetra-
chloride, etc., and can be handled most easily. By filtering
one of these solutions a clear, yellow filtrate was obtained

and by adding acetone there was precipitated a beautiful white powder which was found to contain no sulfur. Repetitions of this experiment with different preparations always gave the same results. Analyses then showed that the product was a hydrocarbon of the same composition as that of the original rubber hydrocarbon, C_5H_8. In benzene it redissolved with the same yellow color and gave no noticeable depression of the freezing point. Its molecular weight must therefore be very large. Finally, it was found that the unsaturation was 57 per cent of that of the rubber hydrocarbon. The other types of products are much more difficult to handle and the results are not so complete as those just given, but they lead to the same conclusions. The reaction, therefore, is an isomerization in the generic sense of the term, with the probable formation of internal cyclic structures.[1]

Note—The reaction in its general aspects is so much like ordinary vulcanization with sulfur that the authors believe that their findings help to substantiate that theory of vulcanization which holds that the first and chief stage is the change in the rubber hydrocarbon to another form, designated by some writers as the "stabile" form, and that the chemical addition of sulfur is a secondary, although probably necessary, reaction to give a more useful practical product.

The unsaturation of these products, as so far determined, varies from 55 to 65 per cent of that of the rubber hydrocarbon. These figures were obtained from the analyses of certain addition products and by the Kemp-Wijs[2] method using iodine-chloride. Calculations from the hydrogen chloride addition products indicate that the hydrogen chloride caused a further decrease in the unsaturation during the preparation of the addition product. The addition of sulfur and oxygen under certain conditions checks very closely the results with the Kemp-Wijs method. The products therefore are probably not identical with those recently reported by Staudinger and Widmer[3] and obtained by the action of zinc and hydrogen chloride on rubber hydrochloride, and of heat on rubber alone,[4] since the unsaturation is higher, but from a comparison of the other chemical and the physical properties there is no doubt but that they all belong to the same class.

Fate of the Reagent

The yields of products are approximately the same as the weight of the rubber used, and this fact is in accord with the theory outlined above. Part of the reagent apparently oxidizes a small amount of the rubber hydrocarbon or, as is more likely, some of the non-rubber constituents, since sulfur dioxide is always evolved. In the case of *p*-toluene-

[1] See Part I, under "Nomenclature."
[2] Kemp, *Ind. Eng. Chem.*, **19**, 531 (1927).
[3] *Helv. Chim. Acta*, **9**, 529 (1926).
[4] Staudinger and Geiger, *Ibid.*, **9**, 549 (1926); Fisher and Gray, *Ind. Eng. Chem.*, **18**, 414 (1926).

sulfonic acid and of β-naphthalenesulfonic acid, toluene and naphthalene have been identified as decomposition products. Much of the reagent remains in the final product either as such or as the ammonium salt or both. The ammonia comes from the decomposition of the nitrogenous constituents in the raw rubber. Extraction with acetone or water will remove them.

Purification and Analysis

The shellac-like products always contain at least a small portion of material which swells but does not dissolve in the solvent. On this account it is best to use dilute solutions (1 to 3 per cent), and even then the filtration is often long and incomplete since the pores of the filter paper become clogged. Much better filtration and more complete recovery of the chief constituent can be had by mixing in fossil flour, using three times the weight of the substance. By further extraction of the residue it is possible to isolate and purify 85 to 90 per cent of the substance as the hydrocarbon. About 5 per cent remains insoluble in the solvent generally used, carbon tetrachloride. The clear, yellow filtrate is allowed to drip slowly into thirty times its volume of acetone, which is stirred mechanically. Beautiful white flocks are formed, which are allowed to settle, washed two or three times by decantation, and then filtered with suction.

If the original reagent was a mixture containing some sulfuric acid,[5] the flocculation takes place readily and the product is a fine white powder which is easily handled. If a very pure sulfonic acid or if a sulfonyl chloride is used then, it is necessary to add a little dilute hydrochloric or sulfuric acid to the acetone in order to cause flocculation. Cooled solutions must be used when the product is low-softening; otherwise it will form a mass which occludes solvent and other impurities. For analytical purposes the precipitates were redissolved, filtered, precipitated two to four times, and finally dried *in vacuo* over concentrated sulfuric acid.

The results of analyses of two representative shellac-like products (thermoprene-SL) prepared from a typical mixture of p-toluenesulfonic acid and sulfuric acid, are as follows:

	CARBON %	HYDROGEN %	TOTAL %
Found (1)	87.95	11.93	99.88
	87.93	11.76	99.69
(2)	87.95	11.76	99.71
	88.20	11.63	99.83
Calcd. for C_5H_8	88.16	11.84	100.00

Chemical unsaturation as compared with rubber hydrocarbon by Kemp-Wijs method: 57.00, 57.31 per cent.

A complete analysis of a similar product prepared as a

[5] Much of the early work was done with p-toluenesulfonic acid prepared according to Lange, D. R. P. 57,391 (1891). This product is a crystalline mixture consisting of approximately 63 per cent of p-toluenesulfonic acid, 12 per cent of sulfuric acid, and 25 per cent of water.

1000-pound batch, pulverized, but only washed and oven-dried, is as follows:

	CARBON %	HYDROGEN %	SULFUR %	ASH %	MOISTURE %	OTHER IMPURITIES INCLUDING OXYGEN[a] %	TOTAL %
Found	85.67	11.46	0.95	0.87	0.53		
	85.62	11.39	0.95	0.83			
Av.	85.65	11.43	0.95	0.85	0.53	0.59	100.00

Calcd. on basis free from sulfur, ash, moisture, and other impurities, including oxygen:

	88.22	11.77					99.99

Calcd. for C_5H_8:

	88.16	11.84					100.00

Chemical unsaturation as compared with rubber hydrocarbon, by Kemp-Wijs method: 57.00, 57.39 per cent.

[a] By difference.

The purification of the shellac-like products prepared with p-toluenesulfonyl chloride gave some difficulty. Chlorine was always found in the purified products. This, however, was due not to chlorination, but to the carbon tetrachloride which could not be removed completely from the samples. A hydrocarbon solvent was not used because no trace of it could then be had and the carbon and hydrogen determination would be much further off.

	CARBON %	HYDROGEN %	TOTAL C AND H %	CHLORINE %	GRAND TOTAL %
(1) Ordinary purification	86.53	11.67	98.20	1.70	99.90
	86.41	11.51	97.92	1.71	99.63
Ratio C:H, 5:7.97					
(2) Very thorough purification, three precipitations, using dilute H_2SO_4 for flocculation	87.38	11.85	99.23		
	87.27	11.63	98.90		
Ratio C:H, 5:8.07					
(3) Same, after having been heated for 90 hours at 150° C. *in vacuo*	87.21	11.86	99.07		
	87.38	11.74	99.12		
Ratio C:H, 5:8.04					
Calcd. for C_5H_8	88.16	11.84			

The original product contained even less chlorine:

	CHLORINE Per cent	
Added as reagent in original mixture (calcd.)	1.69	
Found:		
In product	0.45	0.49
After acetone extraction	0.25	0.19

The gutta-percha-like product (thermoprene-GP) from 7.5 parts of p-phenolsulfonic acid is somewhat soft at ordinary temperatures and gave much trouble in the purification. Even after having been three times dissolved and precipitated, and the solvent slowly removed under diminished pressure in a stream of nitrogen, on the steam bath, the removal was not complete.

	CARBON %	HYDROGEN %	TOTAL %
Found	84.20	11.13	95.33
Calcd. for C_5H_8	88.16	11.84	
Ratio C:H, 5:7.93			

A sample from a larger lot of thermoprene-GP which had only been washed on a mill and dried in an oven gave the following results:

	Carbon	Hydrogen	Sulfur	Ash	Moisture	Other Impurities Including Oxygen[a]	Total
	%	%	%	%	%	%	%
Found	86.15	11.57	0.50	0.27	0.23		
	86.73	11.63	0.47				
Av.	86.44	11.60	0.49	0.27	0.23	0.97	100.00

Calcd. on basis free from sulfur, ash, moisture and other impurities, including oxygen:

	88.16	11.83					99.99

Calcd. for C_5H_8:

	88.16	11.84					100.00

Chemical unsaturation, as compared with the rubber hydrocarbon, by the Kemp-Wijs method, 65.56 per cent.

[a] By difference.

A hard balata type (thermoprene-HB) was prepared from 1000 grams of deproteinized rubber (prepared by steaming a rubber mixture containing sodium oleate and sodium carbonate), 50 grams of concentrated sulfuric acid, and 17 grams of fossil flour, heated in a 1-gallon can in the oven for 6 hours at 149° C. This gave a greater proportion of soluble material than when pale crepe itself was used. A portion was extracted with boiling tetrachloroethane and precipitated twice, yielding 53.8 per cent of the original. It contained no sulfur and no nitrogen. The final sample was reddish brown.

	Carbon	Hydrogen	Total	Ratio C:H
	%	%	%	
Found	82.55	10.75	93.30	5:7.81
	81.99	10.87	92.86	5:7.93
Calcd. for C_5H_8	88.16	11.84	100.00	

The difference from the theoretical in this case may be due to oxygen, since the sulfuric acid mixtures always give off more sulfur dioxide than those with the other reagents. The portion insoluble in the tetrachloroethane analyzed as follows:

	Carbon	Hydrogen	Ash	Total	Ratio C:H
	%	%	%	%	
Found	75.20	9.95	6.56	91.71	5:7.94

German synthetic methyl-rubber-W (warm polymerization product of 2,3-dimethylbutadiene-1,3), in the thermoprene-SL recipe, gave a flexible, shellac-like product which, upon being purified in the regular way and analyzed, gave the following:

	Carbon	Hydrogen	Total
	%	%	%
Found	87.63	12.17	99.80
Calcd. for C_6H_{10}	87.72	12.28	100.00

The purified thermoprenes-SL are soluble, giving clear, yellow solutions in benzene, p-cymene, gasoline, chloroform, carbon tetrachloride, carbon bisulfide, turpentine, tetralin, decalin, and molten camphor. They swell a little in ether,

aniline, and amyl acetate, and are insoluble in methanol and ethyl alcohol, acetone, and glacial acetic acid. Their behavior in the melting point determination varies somewhat with the method of preparation. Generally they soften at 100–5°C., slowly melt at 110–30°C., and at 130–5°C. become amber-colored droplets clinging to the walls of the tube. They are optically inactive. Thin films formed for the determination of the refractive index in the Abbé refractometer were too delicate to be used.

Action of Sulfur

Under the influence of heat sulfur adds chemically to the thermoprenes, converting them eventually into insoluble, hard non-thermoplastics. This change to a non-thermoplastic, like the vulcanization of rubber, can be made by as low as 2 per cent of sulfur, provided the time is extended to 15–20 hours at 141° C., as already mentioned in Part I. However, if they are saturated with sulfur in solution they remain soluble and thermoplastic.

A mixture of 100 parts of the washed and dried thermoprene-SL and 67 parts of sulfur was made on the hot mill. (Only 47 parts of sulfur are required theoretically to saturate the rubber hydrocarbon.) Two samples were heated in an oven at 134–6° C., one (A) for 9 hours and the other (B) for 17 hours. Both were then ground to 60-mesh and extracted with acetone for two full days and nights. A lost 20.71 per cent and B, 21.60 per cent by weight. The extracted samples were dried and analyzed for sulfur:

	Sample A			Sample B	
	Sulfur %	Less 0.95% S in original %		Sulfur %	Less 0.95% S in original %
	22.33			22.74	
	22.24			22.72	
Av.	22.29	21.34	Av.	22.73	21.78

Completely sulfurized rubber $(C_5H_8S)_x$ contains 32.01 per cent sulfur. Since the percentage of sulfur is not a linear function of the amount of unsaturation as compared with the rubber hydrocarbon, in order to determine the percentage of unsaturation from the combined sulfur it is convenient to construct a curve from the theoretical amounts of sulfur combined assuming different per cents of unsaturation. For example, C_5H_8S containing 32.01 per cent sulfur would be 100 per cent unsaturation—that is, one double bond for each C_5H_8 group; $C_{10}H_{16}S$ containing 19.06 per cent sulfur would represent 50 per cent unsaturation; $C_{15}H_{24}S$ containing 13.36 per cent sulfur would represent 33.33 per cent unsaturation; $C_{20}H_{32}S$, 10.53 per cent sulfur, 25 per cent unsaturation; $C_{25}H_{40}S$, 8.61 per cent sulfur, 20 per cent unsaturation, etc. By means of such calculations and the curve drawn from them. it is possible to read off the unsaturation corresponding to a given percentage of sulfur. In this way it can be shown that

A containing 21.34 per cent S represents 57.5 per cent un-
saturation and *B* containing 21.78 per cent S represents 59.0 per
cent unsaturation.

These results correspond very satisfactorily with the figures
found by means of the Kemp-Wijs method—namely, 57.00
and 57.39 per cent—and it is possible, to be sure, that some
substitution took place in the long heating, especially with
sample *B*. These products are non-thermoplastic, but by
heating at 270° C. they can be made thermoplastic again.

The experiments in solution were carried out with the
purified thermoprene-SL (from *p*-toluenesulfonic–sulfuric acid
mixes) in 100 cc. of *p*-cymene with a large excess of sulfur,
and heated in an oil bath for the times and at the temperatures
given in Table I. After the solution had thoroughly cooled
the crystals of sulfur were filtered off and the filtrate was
slowly added to a large volume of acetone. Mineral acids
had to be used to cause flocculation except in *F*. The yields
were sometimes low, even lower than can be accounted for
by ordinary losses due to experimental procedure. Part
of the product apparently was soluble in the acetone; and
this was very noticeable in *D*, where the highest temperature
was used, the product coming out as a varnish which was
purified further by reprecipitation, then forming a dark
yellow powder. The higher temperature in this case may
have caused a change in the unsaturation. The influence
of time and temperature on the amount of sulfur combined
is very definite. Some hydrogen sulfide was always evolved
and probably came chiefly, if not wholly, from the cymene,
since sulfur and cymene alone under similar conditions
gave off hydrogen sulfide.

Table I—Sulfur Experiments in Solution

Expt.	Sub-stance Grams	Sulfur Used Grams	Tempera-ture ° C.	Time Hours	Yield Grams	Sulfur %	Unsatu-ration (Calcd.) %
C	2.0	10.0	170–84	3	1.45	21.15 21.08	57.0
D	1.5	7.5	185–90	3	0.85	17.16 16.47	43.5
E	1.5	7.5	128–36	7	1.40	4.46 4.21	10.3
F	1.7	8.5	87	9 × 24	1.46	1.91 1.89	4.5

Sulfur Chloride

An excess of sulfur chloride usually causes no gel for-
mation until after the mixture has stood for 2 or 3 days, and
even then it is not like the familiar vulcanized-rubber gels.
The products that can be isolated by precipitation with ace-
tone are non-thermoplastic powders.

Seventy cubic centimeters of a 3 per cent carbon tetra-
chloride solution of the purified thermoprene-SL were treated
with 5 cc. of sulfur chloride in 20 cc. of the same solvent,
and after standing a day the product was isolated by pre-
cipitation in the usual manner. Similarly, 2 grams of

the purified thermoprene-SL in 100 cc. of benzene were treated with 10 grams of sulfur chloride. The solution was turbid at first but after remaining stoppered overnight it became clear and more limpid. Three days later it was precipitated in 4.5 liters of acetone. The yield was 2.51 grams. The analytical results were irregular.

	SULFUR %	CHLORINE[a] %
Found:		
CCl₄ solution	16.05	10.61
	16.00	10.52
C₆H₆ solution	17.43	12.13
	17.35	12.09
Calcd. for C₁₀H₁₆SCl	15.72	17.44

[a] Staudinger and Widmer[3] report that in their polycyclo–rubber–sulfur chloride product the chlorine found was only 5.62 per cent. That rubber–sulfur chloride generally shows low chlorine may be due not only to the loss of chlorine as HCl but also to the change in unsaturation of the rubber hydrocarbon by the action of the reagent.

Hydrogen Halides

Early in the work it was expected that the addition products of the hydrogen halides would give the best measure of the unsaturation, but the results varied considerably, possibly because the unsaturation was changed by the action of the hydrogen halides themselves.

HYDROGEN CHLORIDE—The purified chief constituent of thermoprene-SL was used and treated as outlined in Table II. In the first three experiments the substance used, as found out later, was slightly oxidized. The products were isolated in the usual way by precipitation in acetone, and in the first four cases it was necessary to cause flocculation by the use of hydrochloric acid. The products of Nos. 4 and 5 were non-thermoplastic.

Table II—Addition of Hydrogen Chloride

EXPT.	SUBSTANCE Grams	YIELD Grams	CHLORINE %	UNSATURATION[a] %	METHOD OF PREPARATION
1	2.0	2.25	2.65 2.59	5.0	3 hours treatment with dry HCl in 100 cc. CCl₄
2	2.0	1.66	12.37 12.06	26.5	4 hours in 100 cc. C₆H₆
3	2.0	1.64	15.42 15.33	34.5	6 hours in 100 cc. C₆H₆
4	2.0	1.98	8.20 8.16	16.25	3 hours in 100 cc. C₆H₆
5	1.75	1.28[b]	10.17 10.14	21.0	13 days in 100 cc. C₆H₆
6	2.0	1.75	2.18 2.12	4.0	1 day treatment with concd. HCl in 100 cc. CCl₄ on shaking machine

[a] The calculations for the curve for the hydrogen chloride addition product are:

Chlorine %	Unsaturation %
33.91	100.0
20.54	50.0
14.73	33.3
11.48	25.0

For the hydrogen bromide addition product the calculations are:

Bromine %	Unsaturation %
53.64	100.0
36.81	50.0
28.02	33.3
22.62	25.0

[b] Part lost by accident.

HYDROGEN BROMIDE—1.5 grams of the purified thermo-prene-SL were dissolved in 100 cc. of ethylene dibromide and 30 cc. of chloroform (the substance would not all dissolve in the ethylene dibromide alone) and dry hydrogen bromide was passed through the solution for 7 hours. The following day it was precipitated in 3 liters of acetone. The yield was 1.89 grams, consisting of a cream-colored non-thermoplastic product. It was dried over solid potassium hydroxide and concentrated sulfuric acid.

Bromine found, 26.63, 26.54 per cent; which from the curve (Table II, *a*) is equivalent to 30.5 per cent unsaturation.

Halogens

Thermoprene-SL can be halogenated but, as with rubber, there is substitution, even with bromine. The products are non-thermoplastic.

BROMINE—Bromine does not give a good measure of the unsaturation because there is so much substitution, and the bromine titration method[6] for unsaturation as adapted to rubber gave such irregular results that it could not be used.

(1) Two samples of purified chief constituent, which was later found by combustion to contain 5.5 per cent of oxygen, were very slowly treated in carbon tetrachloride solution with a large excess of bromine in the same solvent, at approximately 0° C. Much hydrogen bromide was evolved, and a small amount of a precipitate formed in each case. After filtration and precipitation in a large volume of acetone, the analyses showed unexpectedly concordant results: (*A*) bromine found, 67.34, 67.15 per cent; (*B*) bromine found, 67.36, 67.50 per cent. These amounts of bromine are close to that in rubber bromide, 70.13 per cent, and are much greater than those obtained with the very pure starting material. Whether they hold any significance we do not know.

(2) Two grams of very pure chief constituent in 150 cc. of redistilled carbon tetrachloride were cooled to 0° C., and 3 cc. of bromine in 50 cc. of carbon tetrachloride added during 40 minutes with good stirring. Considerable hydrogen bromide was formed, but no jelly particles separated out. It was then precipitated in 3.5 liters of acetone, filtered, washed by decantation, etc., and dried over solid potassium hydroxide and concentrated sulfuric acid. The product was cream-colored; yield, 3.62 grams. Bromine, 49.37, 49.06 per cent, indicating 41 per cent unsaturation (using a curve as mentioned under sulfur above), on the assumption that there was no substitution. Since there was substitution this figure must be a maximum.

(3) Repetition of (2). The yield was 3.55 grams. Bromine, 51.75, 51.36 per cent, indicating a maximum unsaturation of 45 per cent.

(4) Repetition of (2), but the reaction mixture was allowed to stand in the refrigerator overnight before purifying. Yield, 4.07 grams. Bromine, 57.20, 56.67 per cent, indicating a maximum of 57.3 per cent unsaturation. This figure corresponds closely with the best ones for unsaturation, but is probably fortuitous. It is of interest to note that the yield in this case is 60.7 per cent of the theoretical if we assume 100 per cent unsaturation; that is, $C_5H_8Br_2$ is formed.

6 Lewis and McAdams, *Ind. Eng. Chem.*, **12**, 673 (1920); Fisher, Gray, and Merling, *Ibid.*, **13**, 1031 (1921).

IODINE—Only one experiment was carried out with iodine. One gram of the chief constituent in 50 cc. of carbon tetrachloride was treated with 4 grams of iodine in the same solvent. No hydrogen iodide was noticed. After 2 days it was purified as usual, and it was necessary to use mineral acids to cause flocculation. The yield of a greenish powder was 0.9 gram. Iodine found, 16.37, 16.01 per cent, which, from the curve prepared as with bromine, etc., is equivalent to only 5.5 per cent unsaturation. (This is about the figure obtained for unsaturation by means of the bromine titration.)

Oxidation

AIR—A sample of thermoprene-SL on a watch glass in an air oven at 130° C. gained in weight 3.2 per cent in 71 hours, 5.06 per cent in 304 hours, and 5.63 per cent in 445 hours.

Table III—Air Oxidation at Room Temperature

| | INCREASE IN WEIGHT | | | INCREASE IN WEIGHT | |
TIME	In cabinet (0.2235 g.)	In desiccator (0.2935 g.)	TIME	In cabinet (0.2235 g.)	In desiccator (0.2935 g.)
Days	%	%	Days	%	%
2	0.95	0.14	107	12.48	13.18
7	1.92	..	138	14.94	15.50
11	3.24	..	168	16.24	16.63
18	4.43	0.75	204	17.63	17.88
25	5.86	1.64	291	19.86	18.61
32	6.26	2.45	361	26.44	20.14
39	7.56	3.07	898	34.45 (?)	23.51
46	7.86	3.71	1080	30.02	22.97 (?)
57	9.53	4.84	1261	31.72	23.85
89	11.23	9.64			

In order to determine the air oxidation at room temperature two samples of the chief constituent were allowed to remain on watch glasses—one in a cloth-covered cabinet where it would be free from dust but not from moisture, and the other in a desiccator over concentrated sulfuric acid. The powders were white in the beginning but finally became deep yellow, whereas another sample sealed in nitrogen did not change at all. The theoretical weight increase to form $(C_5H_8O)_x$ is 23.54 per cent. From Table III it is seen that the sample in the presence of moist air went beyond this amount during the time of this experiment, but the one in dry air just reached it and has remained approximately there, not increasing appreciably at the present writing.

A sample that had been dissolved in carbon tetrachloride and had stood for 3 months in a cork-stoppered flask was precipitated with acetone and purified in the usual manner. Upon analysis it was found to have been somewhat oxidized. It contained no ash.

	CARBON	HYDROGEN	TOTAL	OXYGEN (by diff.)
	%	%	%	%
Found	83.09	11.04	94.13	5.87
	83.15	11.02	94.17	5.83

Another sample that had been in gasoline solution in a cork-stoppered, wide-mouth bottle for the same period

of 3 months separated out as a tough gel. This gel was removed, broken up, purified by extraction with carbon tetrachloride, and finally dried and analyzed. It was a yellow powder which was non-tribo-electric, showed no surface tack, and was less thermoplastic than the original. It was ash-free. The analysis indicates 55.24 per cent unsaturation in the original sample, which amount is approximately the same as that found from the addition of sulfur and by the Kemp-Wijs method.

	CARBON	HYDROGEN	TOTAL	OXYGEN (by diff.)
	%	%	%	%
Found	78.00	10.19	88.19	11.81
	78.37	10.35	88.72	11.28
	78.30	10.30	88.60	11.40
Calcd. for $C_{10}H_{16}O$	78.89	10.60	89.49	10.51

PERBENZOIC ACID—It was expected that a titration method for showing the relative unsaturation could be developed with the use of perbenzoic acid, but although some interesting results were obtained in general they varied with the concentration of the reagent and also were irregular and inconsistent. A sample of pure thermoprene-SL was in contact with an excess of perbenzoic acid in chloroform solution for 21 days. It was then precipitated as a white powder with ether—it was soluble in acetone. Analysis indicated it to be $(C_5H_8O)_x$.[7]

	CARBON	HYDROGEN	TOTAL	OXYGEN (by diff.)
	%	%	%	%
Found	71.46	9.41	80.87	19.13
	71.11	9.40	80.51	19.49
Calcd. for $(C_5H_8O)_x$	71.38	9.59	80.97	19.03

A sample of powdered thermoprene-SL (0.6625 gram) was treated similarly for 24 days and the product precipitated with ligroin. Part of it was soluble in carbon tetrachloride and the remainder in chloroform. Both were purified further by re-precipitations. The first had not reached the C_5H_8O stage, and the second had gone beyond it.

PORTION SOLUBLE IN:	YIELD	FOUND	
		C	H
	%	%	%
CCl_4	47.4	74.81	9.52
		75.01	9.52
$CHCl_3$	29.4	71.81	7.90
Total	76.8		

OZONE—This formed a soft, yellow, insoluble product, which upon being boiled with water gave no levulinic aldehyde, and in fact was very stable, not behaving at all like an ozonide. Staudinger and Widmer[3] had a similar experience with "polycyclo-rubber."

POTASSIUM PERMANGANATE—2.75 grams of the chief constituent in 150 cc. of carbon tetrachloride and 5 grams of potassium permanganate in 125 cc. of water were shaken

[7] Compare the formation of rubber oxide $(C_5H_8O)_x$, by Pummerer and Burkhard, *Ber.*, **55**, 3462 (1923).

for 10 days. Upon purification and precipitation with acetone, it was necessary to use dilute sulfuric acid to cause flocculation. The yield of a white powder was low, 0.93 gram. Analysis showed that it contained 2.14 per cent of ash and about 5 per cent of oxygen. The oxidation is evidently incomplete. ($C_{20}H_{32}O$ contains 5.6 per cent oxygen.)

HYDROGEN PEROXIDE—A sample of pure thermoprene-SL treated for 14 days with 3 per cent hydrogen peroxide was shown by titration of the unused reagent to have added 5.4 per cent of its weight as oxygen.

Hydrogenation

Two attempts to hydrogenate the chief constituent in pure ligroin by using hydrogen under 40 pounds pressure at the ordinary temperature and in the presence of reduced platinum oxide[8] were unsuccessful. There was no diminution in pressure after 6 hours in one case and after 15 hours in the other, even though four times as much catalyst was used in the second case. The same conditions caused the reduction of amylene and of rubber. Staudinger and Widmer[3] were also unable to hydrogenate their polycyclo-rubber at the ordinary temperature, although they did obtain a partial hydrogenation at 270° C. and 50 atmospheres pressure.

Attempts to depolymerize or disaggregate the products by heating in a stream of nitrogen for 6 hours at 330° C. and in a sealed tube for 17^1/$_2$ hours at 320° C., and then hydrogenating at room temperature, gave not over 5 per cent reduction. It was not ascertained whether the reduced product was from the original or from decomposition products.

Nitric Acid

The method developed by the senior author for nitrating rubber in solution[9] was used for nitrating the purified thermoprene-SL.

Note—The laboratory procedure is as follows: Five grams of pale crepe dissolved in 100 cc. of carbon tetrachloride are treated with 5.5 cc. of concentrated nitric acid in a glass-stoppered bottle, and the mixture is shaken mechanically for 2 or 3 days. The yellow ochre masses are filtered off with suction, washed with water, and after drying ground to a paste with water, washed, filtered, and allowed to dry. From 5 grams of acetone-extracted rubber 8.27 grams of air-dried product are obtained. The theoretical yield for a nitro-rubber, $C_4H_7NO_2$, is 8.31 grams. The bright yellow product is slightly hygroscopic; it is soluble in acetone, aniline, pyridine, acetic anhydride, nitrobenzene, and aqueous sodium hydroxide, giving a deep maroon color in the latter. The unsaturation, determined on a 1 per cent nitrobenzene solution by the Kemp-Wijs method, was 24.8 per cent of the unsaturation of a nitro-rubber hydrocarbon. It is very probable that the nitric acid has caused the change in unsaturation just as the other acids do. The product therefore is probably a nitro-polycyclo-rubber. The substance is unstable toward heat and is difficult to analyze. Found:

[8] Adams, *et al.*, *J. Am. Chem. Soc.*, **44**, 1397 (1922); **45**, 1071, 2171 (1923).

[9] U. S. Patent, 1,609,806 (1926).

N = 12.01 per cent, calcd. N = 12.38 per cent (but this result has not yet been duplicated). This work will be published more completely later.

On the assumption that a substance with the composition $C_5H_7NO_2$ was formed, the yield was practically quantitative. The product is a yellow amorphous powder, only partially soluble in acetone, and turns red-brown without dissolving very much in aqueous alkalies. It is much more stable when heated than the corresponding nitrated rubber. In a melting point tube it darkened at 168° C., became red-brown at about 200° C., but was not completely melted at 260° C. As with nitrated rubber the analytical results were not entirely satisfactory. Nitrated thermoprene-GP was non-thermoplastic, but completely soluble in aqueous alkali with the characteristic deep maroon color.

Heat

Thermoprene-SL is more stable toward heat than rubber, the decomposition into volatile products being practically none under 350° C. Staudinger and Widmer[3] found it necessary to heat to 350–450° C. to obtain any decomposition of their polycyclo-rubber. Carbon tetrachloride solutions of the heated thermoprenes when poured into acetone gave no precipitates, and the addition of mineral acids caused no flocculation although gummy materials finally did settle out.

Action of Other Reagents on Rubber

In order to determine whether the reagents already mentioned are the only ones that produce these changes in rubber, many other types of substances were milled into rubber and the mixtures heated similarly—that is, 15 to 20 hours at 125–45° C. None of them, however, gave products like those described above. It is of interest to note that selenic and benzeneselenonic acids showed a slight "vulcanizing" action, but phosphoric and arsenic acids, and organic phosphonic, arsonic, and siliconic acids gave only soft sticky masses. In the list that follows the figures in parentheses refer to the concentration of the reagent if other than 10 parts to 100 of rubber:

p-Toluene sulfinyl chloride gave a black, stiff, non-thermoplastic, rubbery mass; p-toluenesulfinic acid gave a black, resilient product; tetrachloroquinone (chloranil) (20) gave a product like "short," soft-vulcanized rubber; picryl chloride (20), a product which was black, shiny, and like overvulcanized rubber; p-tolylmercuric chloride (30) gave a soft sticky product, and mercury-p-ditolyl (30), heated 48 hours at 148° C., gave a resilient mass; selenic acid (6 and 15) gave rubbery products; benzene selenonic acid (20) acted similarly, but selenious acid made no apparent change.

Concentrated hydrochloric acid (30) mixed with fossil flour, heated 20 hours at 175° C., gave a soft-vulcanized product.

Phosphoric acid, sirupy, even up to 20 parts with fossil flour, and heated 6 hours at 200° C., gave only soft, sticky masses. Similarly with arsenic acid, and the organic phosphonic, arsonic and siliconic acids, such as p-toluenephosphonic, α-phenyl-β-

benzoylethylphosphonic acid, *p*-toluenearsonic, *p*-phenolarsonic, *p*-nitrophenolarsonic, arsanilic (40), and toluenesiliconic acid.

The following gave only soft, sticky masses: *p*-toluene sulfonamide (40), diphenyl sulfone (20), di-(*p*-hydroxyphenyl)-sulfone (20), sulfonal, phenyl *p*-toluene sulfonate, *o*-benzoic sulfinide (saccharin) (20), sodium salts of several simple sulfonic acids, 1,8-naphthyl sultone, oxalic acid, phenol (40), tribromophenol (40), *α*- and *β*-naphthol (40), nitroso-*β*-naphthol, trioxymethylene (40), trioxymethylene (15, mixed with aniline sulfate, 2), phthalic anhydride (30), hexamethylenetetramine (40), methylene-amino-aceto-nitrile (40), *p*-nitrobenzoyl chloride, diphenylcarbamide chloride, acetone sodium bisulfite, sodium bisulfite, potassium bisulfite (50), potassium bisulfate (40), sodium ferrocyanide (40), cupric sulfate, cryst. (40), nickel sulfate (40), gypsum (50), uranium acetate (40), chromic anhydride (20), stannic oxide (20), molybdic acid (20), vanadic acid (20), titanic acid (20), and tungstic acid.

Acknowledgment

Part III

Methods of converting rubber in solution into similar thermoplastic and non-thermoplastic isomers will be given in a later paper.

Rate of Cure of Reclaimed Rubber

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Data are presented emphasizing the well-known fact
that reclaimed rubber vulcanizes at a much more rapid
rate than new rubber, and that, even in small concentra-
tion, in a new rubber stock it materially increases the
rate of cure. Possible reasons for this are discussed and
experimental evidence given to show the influence of the
residual alkali in the reclaim, and the effect of the heat
treatment in itself. Neither of these explains the rapid
rate. The need for, and methods of, compensating for
this rapid rate of cure in compounding with reclaimed
rubber are discussed, with especial emphasis on the influ-
ence of the rapid rate of cure on the aging characteristics
of a stock.

I N SPITE of the enormous importance of reclaimed rub-
ber the literature on this material, aside from patents,
is extremely meager.   Especially is this true with refer-
ence to the properties and methods of using reclaimed rubber.
Such properties as tensile, elongation, resistance to tear, and
resistance to wear, both of reclaimed rubber itself and of
products in which reclaimed rubber has been combined with
new rubber, have been discussed at considerable length in
recent publications[1,2,3] and also as far back as 1902,[4] but
the rate of cure of reclaimed rubber, which is of paramount
importance in connection with the proper re-use of reclaim
has received little or no mention.   In the controversy be-
tween Ditmar[5] and Alexander[6] concerning the chemical

[1] Holt and Wormeley, *Bur. Standards, Tech. Paper* **294** (1925).
[2] Bierer and Davis, *Ind. Eng. Chem.*, **18**, 348 (1926).
[3] Winkelmann, *Ibid.*, **18**, 1163 (1926).
[4] Weber, *India Rubber J.*, **23**, 511, 561 (1902).
[5] *Gummi-Ztg.*, **21**, 694, 730 (1907).
[6] *Ibid.*, **21**, 708 (1907).

identity of regenerated rubber and vulcanized rubber, the former asks, "How else does Alexander explain the fact that reclaimed rubber vulcanizes much more quickly than raw rubber?," and Alexander replies, "I do not know that this fact has yet been established by exact experiments and I doubt if it can be accepted as generally true." And still today, as far as the writers are aware, no proof of this rapid rate of cure appears in the literature. Bierer and Davis,[2] Winkelmann,[3] Weber,[7] and Palmer[8] all refer to the physical properties of very short cures of reclaim-sulfur mixtures, without commenting on the short length of these cures as compared with those necessary when new rubber is used with a similar concentration of sulfur. Winkelmann[3] shows that the rate of cure of reclaimed rubber is influenced but slightly by organic accelerators, experimentally confirming an anonymous statement to that effect made several years earlier.[9] Alexander[6] and Pickles[10] advanced possible causes for the increased rate of cure in the presence of reclaim, but gave no experimental data. Apparently the "two of the largest tire manufacturers in the country," which furnished Holt and Wormeley[1] with the compounds for their work on the wear resistance of tire treads containing reclaimed rubber, were unaware of the rapid rate of cure of reclaimed rubber, or else completely ignored it, for even though introducing into their formulas as much as 25 per cent of reclaim, the sulfur content, already high (4.9 per cent), was not reduced and the accelerator concentration actually increased.

Inasmuch as the literature afforded no experimental data on the rate of cure of reclaimed rubber versus new rubber, the writers have undertaken to fill this gap. In Figures 1, 2, and 3 are plotted data on samples of whole-tire, carcass, solid-tire, and tube reclaims, when tested against new rubber (smoked sheets). In this work 5 per cent of sulfur was added to the whole-tire reclaim and the corresponding amount based on the respective rubber contents was added to each of the other reclaims and to the smoked sheets. The actual proportion of sulfur to rubber in each case was 8.3 per cent.

In the writers' opinion the relationship between the rates of cure in these mixtures is best seen in Figure 1. With increase in curing time these so-called "modulus" curves rise to a peak and then fall off. In other words, the stress required to produce a given elongation increases with cure up to a maximum, beyond which a decrease in stress occurs— i. e., a lesser load is required to produce the same elongation. Without entering into the controversy as to the best method of selecting the "optimum" cure,[11] the writers have arbitrarily chosen to use the peak in the curve in which time

[7] "Chemistry of Rubber Manufacture," Charles Griffin and Co., Ltd. (1926).

[8] *Ind. Eng. Chem.*, **19**, 1030 (1927).

[9] *Caoutchouc & gutta-percha*, **15**, 9512 (1918).

[10] *India Rubber J.*, **60**, 957 (1920).

[11] Wiegand, *Ind. Eng. Chem.*, **18**, 1157 (1926).

of cure is plotted against stress at a given elongation as the point of reference in comparing rates of cure. This has been selected in preference to the peak in the tensile-time, or tensile product *vs.* time, curve, inasmuch as the points on these latter curves are more difficult to determine accurately, owing to the fortuitous and erratic nature of the breaking point.

Judging from the peak in the modulus curves of Figure 1, all the samples of reclaim are very much faster in curing rate than smoked sheets, whether the latter are cured in the presence or absence of zinc oxide. The floating-tube reclaim (alkalinity as NaOH 0.12 per cent) reaches its maximum modulus in 1 hour, the whole-tire reclaim (alkalinity 0.10 per cent) in 1 hour and 10 minutes, and the carcass reclaim (alkalinity 0.10 per cent) also in 1 hour and 10 minutes. The solid-tire reclaim (alkalinity 0.016 per cent), which was the only one of the four reclaims made
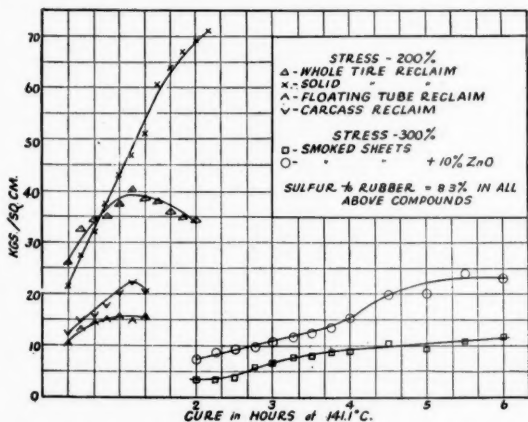

Figure 1—Stress at Given Elongation *vs.* Time of Cure of Reclaim and New Rubber

without the use of alkali, is appreciably slower in curing rate as judged by the peak in the curve. The 200 per cent modulus curve is still rising at the end of 2 hours and 10 minutes; beyond that cure rupture occurred below an elongation of 200 per cent, but the 100 per cent elongation figures (not shown in the graph) on longer cures show that the peak was reached in 2 hours and 10 minutes.

In the case of the new rubber in the absence of zinc oxide no definite peak is reached with smoked sheets in 6 hours; in the presence of 10 per cent of zinc oxide the peak occurs apparently at 5 hours and 30 minutes. In other words, the slowest curing reclaim—i. e., the solid-tire reclaim—reached its optimum cure in less than half the time required by the smoked sheets containing 10 per cent of zinc oxide, while the fastest curing sample of reclaim—the tube reclaim—cured to optimum modulus in almost one-sixth the time.

This remarkably fast rate of cure of reclaimed rubber persists to a surprising extent when reclaim is introduced as a compounding ingredient. This is very clearly shown in Figure 4, where the modulus curve for a practically pure gum mixture (I) accelerated with di-*o*-tolylguanidine is shown compared with a similar stock containing 15 per cent of carcass reclaim of 90 per cent rubber content (II). The pigments present in the reclaimed rubber were compensated for, so that there was no increase in pigmentation. In this replacement guayule was treated as all rubber, and subsequent tests show that this did not influence the result.

Table I—Stress at 100% Elongation
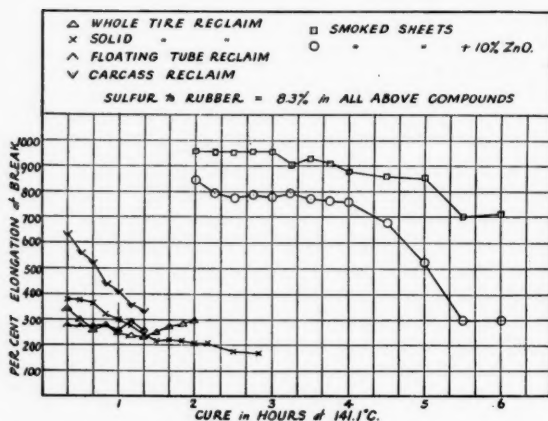(Kg. per sq. cm.)

130 min.	150 min.	170 min.
38	35.5	37.5

Figure 2—Elongation *vs.* Time of Cure Curves of Reclaim and New Rubber

		II
Carcass reclaim	....	16.3
Smoked sheets	96.5	83.6
Guayule	3.5	....
Sulfur	3	3
Zinc oxide	2.75	1.2
Mineral rubber	3.25	3.25
Di-*o*-tolylguanidine	0.5	0.5
	109.50	107.85

In spite of the quite high organic accelerator content in both cases, the mixture containing the reclaim shows a much more rapid rate of cure, reaching its optimum in 45 minutes at 143.4° C. as compared with 60 minutes for the mixture containing no reclaim. Perhaps even more striking is Figure 5, in which a practically pure gum mixture (III) accelerated with aldehyde ammonia is shown with 5 (IV), 10 (V), and 15 (VI) per cent of carcass reclaim. As is seen from the formulas, in introducing the reclaim for rubber the rubber in the reclaim (calculated as 87 per cent rubber)

replaces smoked sheets, and the pigment in the reclaim is taken out of the zinc oxide.

	III	IV	V	VI
Carcass reclaim	....	5	10	15
Smoked sheets	69.5	65	60.75	56.5
No. 3 amber crepe	10	10	10	10
Caucho ball	7	7	7	7
Guayule	4	4	4	4
Sulfur	3	3	3	3
Zinc oxide	2.5	2	1.25	0.5
Aldehyde ammonia	1	1	1	1
Liquid asphalt	3	3	3	3
	100.0	100.0	100.0	100.0

While the mixture containing no reclaim had apparently not reached its optimum within 90 minutes at 132.2° C., that containing 5 per cent of reclaim reached its optimum in 60 to 75 minutes, that containing 10 per cent in 45 to 60 minutes, and that containing 15 per cent in 30 minutes.

In highly pigmented compounds, such as treads, the influence of reclaim on the rate of cure is somewhat masked by the high pigmentation, and therefore larger amounts of reclaim are necessary in illustrating its effect on rate of cure. In Figure 6 a highly compounded tread is shown containing
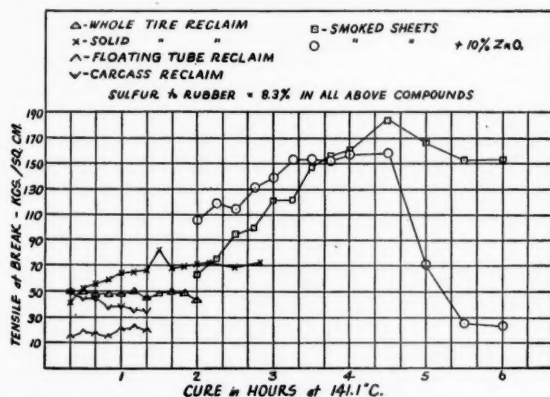

Figure 3—Stress at Break *vs.* Time of Cure Curves of Reclaim and New Rubber

5 per cent (VII) and 35 per cent (VIII) of whole-tire reclaim. While the 5 per cent reclaim stock reached its optimum cure in 90 to 105 minutes at 143.4° C., the corresponding mixture containing 35 per cent of reclaim reached its optimum in 60 minutes.

	VII	VIII
Smoked sheets	60	21.5
Amber crepe	30	30
Rolled brown crepe	10	10
Whole-tire reclaim	9	62
Zinc oxide	10.75	2
Sulfur	3	2.75
Gas black	48	41.5
Pine tar	7	5.25
Di-o-tolylguanidine	1	0.95
	178.75	175.95

Possible Causes of Rapid Rate of Cure

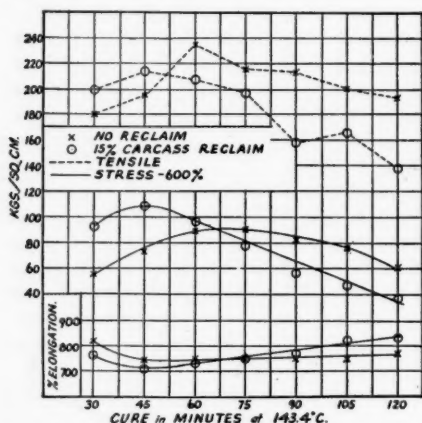As far as the writers are aware, the cause or causes for this rapid rate of cure of reclaimed rubber have never been investigated. In the case of alkali reclaims it is logical to assume that residual alkali plays a part, for it is well known that sodium and potassium hydroxides and carbonates are active accelerators of vulcanization, as has been shown by Martin,[12] Eaton,[13] van Heurn,[14] and others. This is the opinion of Pickles,[10] who writes in 1920: "Some firms are just learning now that reclaim made under the alkali process possesses considerable accelerating power, but this is probably because a certain amount of caustic potash is still left in the rubber even after washing and drying." Residual accelerator, other than caustic, might also be responsible for the rapid rate of cure. This is also the opinion of Alexander,[6] who attributes the rapid rate of cure of certain reclaimed rubbers to the presence of litharge in the scrap from which it was made. These, however, are only two of the possible causes for the rapid rate of cure of reclaimed rubber.

Figure 4—Effect of Carcass Reclaim on Rate of Cure of Friction Compound I

During the process of reclaiming, rubber is subjected not only to very high temperatures, upward to 191.9° C. (175 lbs. steam pressure), but also to excessive milling or mechanical working. Following the high temperature "cook" in an autoclave, the rubber, after drying, is mechanically worked on mills until the scrap has knit together. It is then transferred to refiners, which consist of two heavy rolls set very close together, where the reclaim is milled out into a thin sheet to remove the coarse, incompletely devulcanized pieces of rubber known as "tailings." The result of this working, both at the massing mill and the refiner, is a marked increase in plasticity. Both heat and mechanical working have been shown to increase the reactivity of the rubber hydrocarbon. Axelrod[15] found that heating Para rubber for even so short a period as 30 minutes at 120° C. caused it to take up sulfur at a faster rate, as shown by the vul-

[12] "Rubber Industry," p. 205 (1914); *J. Soc. Chem. Ind.*, **34**, 725 (1915).
[13] *Agr. Bull. Federated Malay States*, **4**, 162 (1916).
[14] *Neth. Gov. Inst. Bull.*, Pt. VI, 201 (1916).
[15] *Gummi-Ztg.*, **24**, 352 (1909).

canization coefficient after a given time of cure. The exact conditions under which the rubber was heated are not clear. The same author also compared the rate of cure of washed Para rubber before and after working on a mixing mill. He again found that the sulfur added more rapidly to the rubber which had been milled. Harries[16] has stated that rubber which has been heated in xylene, or which has been thoroughly masticated, shows a marked increase in reactivity toward permanganate, "apparently having become depolymerized" by these treatments. Staudinger and Fritschi[17] found it necessary in order to hydrogenate rubber to use both high temperature and high pressure, while Harries[18] was successful in hydrogenating rubber at ordinary temperatures only when he first subjected the rubber to strong plasticization. Fisher and Gray[19] have shown that neither heating rubber nor masticating it results in a higher degree of unsaturation, as judged by its ability to take up iodine. In fact, when these investigators heated pale crepe in a steel tube for 7 hours at 285–300° C., temperatures in excess of those ordinarily used in the devulcanization of rubber, they found a decrease in the unsaturation of the material. Their results strongly indicate that heat and mastication do not depolymerize rubber in a chemical sense, but rather produce a physical disaggregation, which would increase the reactivity of the rubber due to decrease in the size of the particle, and therefore increase in the surface. However this may be, analogy certainly would indicate that the increased rate of cure of reclaimed rubber may be caused by the action of heat and mastication.

Again, the increased rate of cure might be ascribed to the "head start" of the reclaim with respect to chemical state of cure. Whole-tire reclaim ordinarily contains approximately 3 per cent of combined sulfur. Allowing for the pigment, softener, and other non-rubber substances, this combined-sulfur content amounts to approximately 5 per cent of the rubber. While this figure does not represent the actual amount of sulfur combined with the rubber, as some of the combined sulfur is undoubtedly combined with pigment, resins, etc., it does indicate very definitely that the sulfur coefficient is very high. It is conceivable, therefore, that reclaimed rubber with such a high coefficient of vulcanization might require the addition of less sulfur to bring it back to the vulcanized elastic state, in which case it should not take so long to cure it.

A further viewpoint is that oxygen may play a part. The scrap from which reclaimed rubber is made contains the rubber in a partially perished and oxidized condition. During the devulcanization process some air is ordinarily present and it is probable that a certain amount of oxygen combines

[16] *Ann.*, **406**, 198 (1914).
[17] *Helv. Chim. Acta*, **5**, 785 (1912).
[18] *Ber.*, **56**, 1050 (1923).
[19] *Ind. Eng. Chem.*, **18**, 414 (1926).

with the rubber during the devulcanization process at high
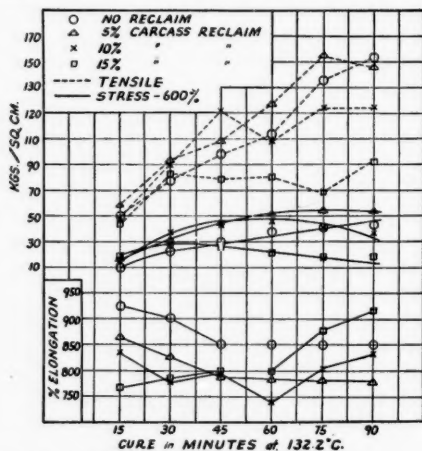temperature. That such oxidation products could in-

Figure 5—Effect of Carcass Reclaim on Rate of
Cure of Friction Compound III

fluence the rate of cure is not inconceivable, for it is well
known that rubber undergoes a sort of "vulcanization"
under the influence of oxygen. This has been clearly shown
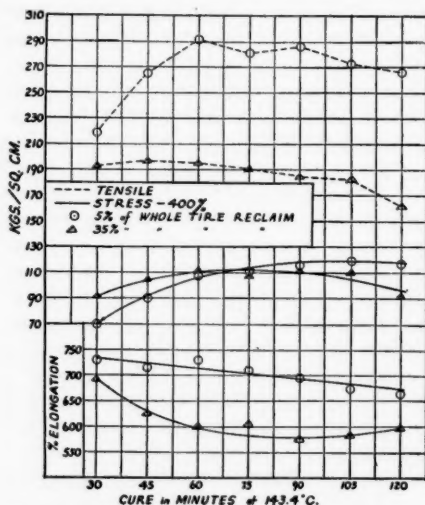by the work of Ostromuislenskii,[20] who has effected such a

Figure 6—Effect of Whole-Tire Reclaim on Rate
of Cure in Tread Compounds VII and VIII

change through the use of polynitro compounds or benzoyl
peroxide.

Still other theories might be advanced, such, for example,

[20] *J. Russ. Phys. Chem. Soc.*, **47**, 1453, 1462, and 1467 (1915); *J. Soc.
Chem. Ind.*, **35**, 59 (1916).

as that the "polyprene sulfide" acts as a catalyst for the combination of sulfur with new rubber—but the five possibilities enumerated below are certainly the most logical for investigation:

(1) Residual alkali in the reclaim
(2) Unchanged accelerator in the reclaim
(3) Depolymerization by the action of heat and mastication
(4) "Head start" of the reclaim with respect to chemical state of cure
(5) Oxidation products acting as curing agents

The experimental data presented in this paper are confined to work carried out to determine whether, and to what extent, residual alkali, heat, and the chemical state of cure are responsible for the rapid curing rate of reclaimed rubber.

Residual Alkali

Though the presence of alkali has previously[10] been advanced as the reason for the rapid rate of cure of reclaimed rubber, no conclusive data are available. With the purpose of settling this point, reclaimed rubber of known alkali content was used in compounding mixture IX. The sample of reclaim used was a whole-tire reclaim of the following composition:

	Per cent		Per cent
Acetone extract	10.60	Zinc oxide	10.0
Total sulfur	2.82	Clay	10.5
Free sulfur	0.07	Carbon black	6.0
Alkalinity (as NaOH)	0.10	Rubber content (by	
Ash	20.53	difference)	60.0

On the basis of this analysis, a control compound, X, was made up containing no reclaimed rubber but all smoked sheets compounded with the pigments present in the reclaim together with the added zinc oxide, sulfur, and accelerator used in compound IX.

	IX	X
Smoked sheets	100	100
Reclaim	75	...
Sulfur	4	3
Di-o-tolylguanidine	1	0.7
Zinc oxide	10	12
Clay	...	5.5
Gas black	...	3
Liquid asphalt	...	4
	190.0	128.2

In order to show the effect of added alkali, three other compounds based on X were included. These contained, respectively, 0.06, 0.12, and 0.18 per cent of caustic soda to the rubber. The alkalinity of the reclaim (0.10 per cent) corresponds to 0.053 per cent of sodium hydroxide to the rubber in compound IX. Thus, the mixture containing no reclaim but 0.06 per cent of sodium hydroxide to the rubber was fully equivalent in alkali content to the mixture containing the reclaim. The alkali was added to these batches in the form of a 2.4 N solution; it was added to the batch toward the end of the mixing period after all the dry pigments had been thoroughly incorporated.
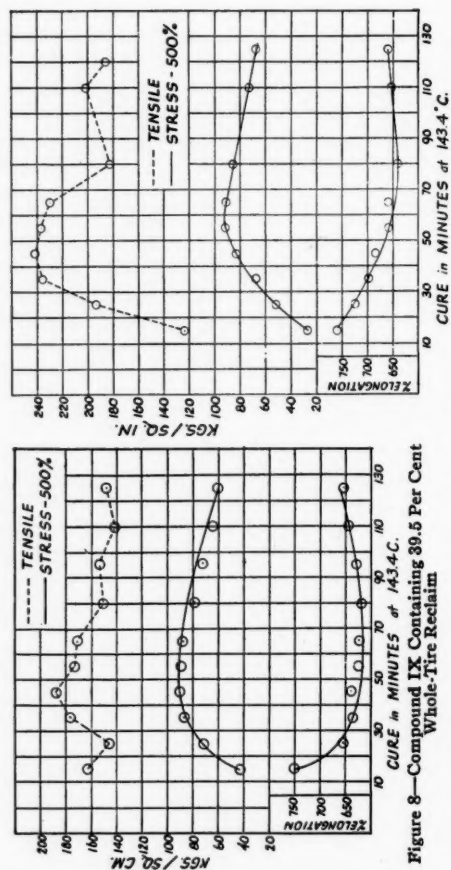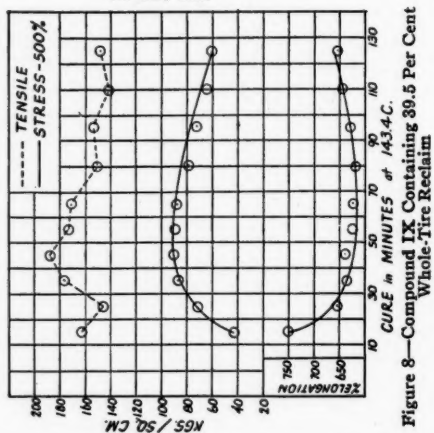
Figure 7—Compound X with No Additional Alkali

Figure 8—Compound IX Containing 39.5 Per Cent Whole-Tire Reclaim
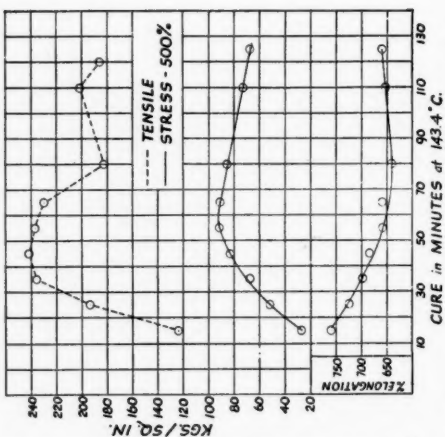
Figure 9—Compound X with 0.08 Per Cent NaOH to Rubber

Effect of Whole-Tire Reclaim vs. Added Alkali in Compound

The results of this work are plotted in Figures 7 to 11. From these curves it is clear that, although the addition of 0.06 per cent of caustic did accelerate the cure of the new-rubber mixture, the rate did not equal that of the mixture containing 39.5 per cent of reclaim. This is clearly seen by comparing the time required in each case to reach the peak in stress at 500 per cent elongation. Even with 0.18 per cent of caustic to the rubber, which is more than three times that present in the mixture containing reclaim, the rate of cure is not equal to that of the mixture containing the reclaim.

Further proof that the alkali content of reclaim accounts at least only partially for the rapid rate of cure was obtained as follows: Scrap for use in reclaiming was made from quality tread XI and carcass XII. The tread was cured for 90 minutes at 143.4° C.; the carcass for 75 minutes at the same temperature. A 50:50 mixture of these two cured compounds constituted the scrap. This was then reclaimed in a small laboratory devulcanizer (Figures 12 and 12A),[21] consisting of a steel bomb 1.27 cm. thick with a capacity of 3.8 liters. It is shown in an inverted position, in which position it is operated. The charge consisted of 1 kg. of scrap and 2.2 liters of liquid. The heating was done electrically and a moderate amount of agitation produced by mounting the bomb and furnace on a revolving support and providing a rocker arm, actuated by a motor-driven eccentric. With this autoclave reclaims could be made which duplicated very satisfactorily factory-scale products.

From the scrap described above, two separate batches of reclaim were made, using a 9-hour cook at 182–185° C. In one case the liquid used was water, and in the other 8 per cent caustic soda solution. The alkali cook, after washing, drying, and refining, showed an alkalinity of 0.01 per cent. These two reclaims were then used to the extent of 10 per cent in compounding a tread mixture quite similar to the tread used as scrap in manufacturing the reclaim, except that it contained 10 per cent of the reclaim. Compound XIII contains the alkali-cook reclaim, while compound XIV contains the water-cook product.

	XI	XII	XIII	XIV
Smoked sheets	53	100	57	57
Amber crepe	36	...	33	33
Rolled brown crepe	11	...	10	10
Water-cook-reclaim (50:50 XI and XII)	...	...	...	20.4
Alkali reclaim (50:50 XI and XII)	...	...	20.4	...
Sulfur	2.9	3	3.2	3.2
Di-o-tolylguanidine	0.7	0.5	0.7	0.7
Zinc oxide	36.5	2.75	32.5	32.5
Gas black	32.5	...	39	39
Mineral rubber	...	3.25	...	...
Pine tar	5.25	...	8	8
	177.85	109.50	203.8	203.8

In Figure 13 are plotted the modulus curves of the two mixtures (XIII and XIV). Figure 14 gives curves showing the influence of 0.06 and 0.12 per cent of caustic soda to the

[21] Designed by Roy W. Brown, of the Firestone Engineering Laboratory.

total rubber in compound XIV. It is clear that there was no appreciable increase in rate of cure where the alkali reclaim was used, and that the addition of up to 0.12 per cent of alkali to the rubber did not materially affect the rate. This experiment is of interest as showing, not so much the effect of different concentrations of alkali, for the actual difference in the alkali content of the reclaims prepared by the two methods was very small, but as showing that the use of alkali in the cook does not bring about changes which appreciably affect the rate.
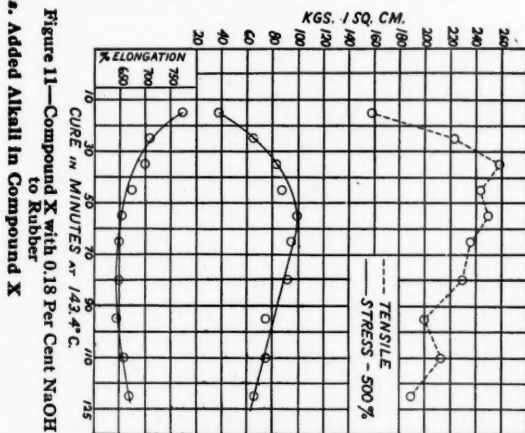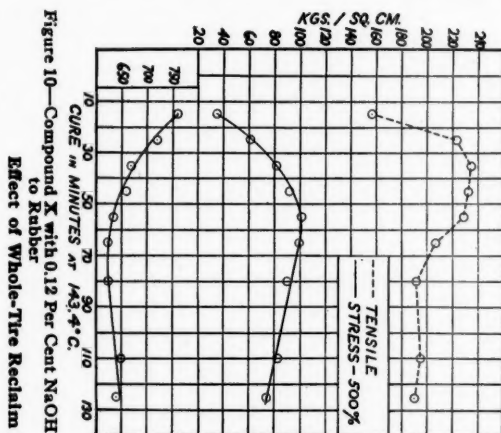
Action of Heat

In order to determine the extent, if any, to which the devulcanization temperatures are responsible for the rapid curing rate of reclaimed rubber, a series of experiments in the experimental autoclave was undertaken in which pale crepe was subjected to various temperatures, including that ordinarily used in devulcanization. Water was used as the heating medium. The pale crepe was a sample that had been thoroughly blended on a mill and then cut into small pieces in order to expose a large surface. One portion was subjected to a temperature of 93.3° C. for 6 hours; a second sample of this same rubber was heated at 137.7° C. for 6 hours; still a third was heated at 185° C. for 6 hours. To give a more complete picture of the behavior at 185° C., samples were also run at this temperature for 3 and for 9 hours, respectively. In Figure 15 are seen the results of compounding these different heat-treated samples in formula XV.

	XV
Pale crepe	100
Sulfur	3
Zinc oxide	3
Di-o-tolylguanidine	0.5
	106.5

A sample of this same pale crepe, which had been soaked in water for 24 hours at 60° C., was also included. The water extract of the pale crepe was 2.63 per cent; after soaking at 60° C. the extract was 1.35 per cent. From Figure 15 it appears that this soaking increased the rate of cure of this rubber—why, the writers do not know. A somewhat similar increase in physical properties and rate of cure has been recorded without explanation by van Heurn.[14] From these curves it is clear that by keeping the time of treatment constant (6 hours) and increasing the temperature, there resulted little or no change in rate of cure as judged by the optimum in the curves. The higher the temperature, the lower was the modulus. If anything, the sample of rubber which was subjected to a temperature no higher than 60° C. has the fastest rate of cure; hence, it would appear that the high temperature used in devulcanization plays a very small part in the rapid rate of cure of reclaimed rubber. Considering the curves which represent the three different time intervals of heating at 185° C., it is interesting

to note that after 3 hours' heating there was practically no change in the modulus obtained or in the rate of cure.

It is worthy of note in connection with the tensile-strength results shown in Figure 16 that up to 137.7° C. the heat treatment had very little effect on the tensile strength of the rubber, while the rubber subjected to a temperature of 185° C., even for 3 hours, lost appreciably in tensile strength.

Figure 10—Compound X with 0.12 Per Cent NaOH to Rubber

Figure 11—Compound X with 0.18 Per Cent NaOH to Rubber

Effect of Whole-Tire Reclaim *vs.* Added Alkali in Compound X

Three and 6 additional hours at this temperature did not lower the tensile figures. Winkelmann,[3] working with a vulcanized tread compound, found that the decrease in tensile had reached a maximum in 4 hours or less at 135° C.

Influence of Combined Sulfur

If there is anything to the theory that the rapid rate of cure of reclaimed rubber is connected with its chemical "head start" then the combined-sulfur content of a reclaim should be an important factor in the rate of cure. In order

to throw light upon this point, scrap for reclaiming was made from the two following compounds, which differ only in sulfur content:

	XVI	XVII
Smoked sheet	100	100
Sulfur	3	1.5
Zinc oxide	2	2
Magnesium oxide	2	2
Tetramethylthiuram disulfide	0.27	0.27
	107.27	105.77

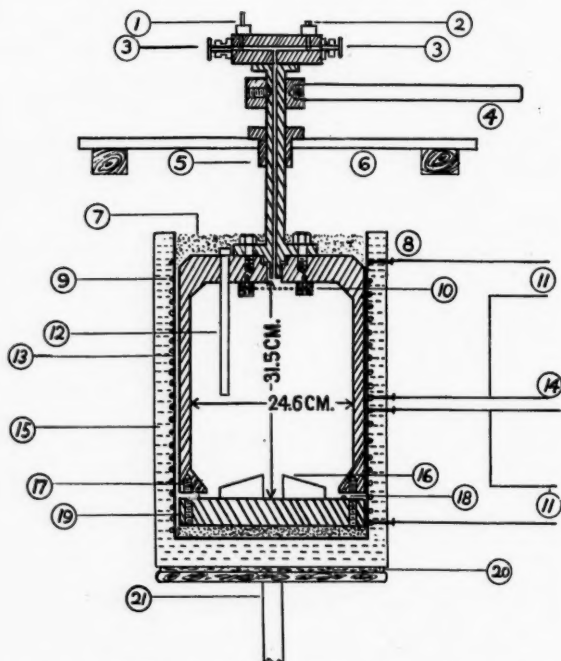**Figure 12—Experimental Devulcanizer**

1—Blow-off line	12—Thermocouple well
2—Pressure-gage connection	13—Copper cylinder, asbestos-covered
3—Valves	
4—Rocker arm	14—Series connection switch
5—Bearing	15—Magnesia pipe covering
6—Support	16—Agitator fins
7—Asbestos fiber	17—Bolt circle
8—Electrical connection	18—Lead gasket
9—Chromel-wire heating element	19—Lid
10—Removable screen	20—Asbestos board
11—Alternating-current source (110 volts)	21—Revolving stool

Each compound was cured for 20 minutes at 132.2° C. and then comminuted to the approximate size of ordinary whole-tire scrap and heated in the experimental devulcanizer in water for 8 hours at 185° C. The respective reclaims were then dried and refined in the usual manner. These reclaims, which had a combined-sulfur content of 2.5 and 1.4 per cent, respectively, were tested in two types of compound, a pure gum (XVIII) and a tread (XIX).

	XVIII	XIX
Smoked sheets	100	100
Sulfur	3	2.5
Zinc oxide	5	14
Di-o-tolylguanidine	0.7	0.7
Gas black	...	40
Clay	...	3
Pine tar	...	7
	108.7	167.2

Using XVIII as the control, two mixtures were made up in which 27.2 parts of the smoked sheets were replaced by the respective reclaims. This gave a reclaim content of 25 per cent. Since the pigmentation of these special reclaims was very low, no allowance was made for their pigment content. Figure 17 shows the load required to produce an elongation of 500 per cent over a range of cures. It is seen that the peak in each curve occurs at the 60-minute cure at 143.4° C. Both compounds containing the reclaim are much stiffer than the compound containing all new rubber. This is typical of the effect of reclaimed rubber on modulus. The above results have been checked, so apparently the combined sulfur of the reclaim had very little to do with the rate of cure.

When these reclaims of different combined-sulfur content were introduced into tread compound XIX to the extent of 18 per cent (30 parts), an equal weight of rubber was removed since these reclaims contained practically no fillers. The results are shown in Figure 18. While the indications are that the higher sulfur reclaim has produced a slightly faster rate of cure, the figures are not considered conclusive in view of the clean-cut results obtained with the pure-gum mixtures. However, the high-sulfur reclaim used contained only 2.3 per cent of combined sulfur to the rubber, whereas the majority of commercial reclaimed rubbers will run very much higher—in the case of whole-tire reclaim close to twice that amount. Further work has therefore been started in which the differential between the high- and low-sulfur reclaim is much greater, and the high-sulfur reclaim approaches more closely the commercial product in sulfur content.

Commercial Aspects

The rapid rate of cure of reclaimed rubber may be an asset or a liability depending upon the use to which the reclaim is to be put. Inasmuch as accelerators are added to practically all commercial rubber mixes to hasten the cure, it would seem to be a very desirable property. However, where rapid rate of cure is desired and obtained through the use of accelerators, it is usually controllable; this is not always the case, but by reducing the concentration of most accelerators the rate may be reduced, and if this is not effective, as in the case of certain of the ultra-accelerators like the tetramethyl-thiuram mono- and di-sulfides, the concentration of sulfur may be reduced.

In mixtures containing any appreciable amount of reclaim

such changes are quite ineffective, as Winkelmann[3] has pointed out. In Figure 19 are plotted data showing the effect of reducing to the extent of 10 per cent the sulfur in pure-gum formula II. This reduction from 3.0 to 2.7 per
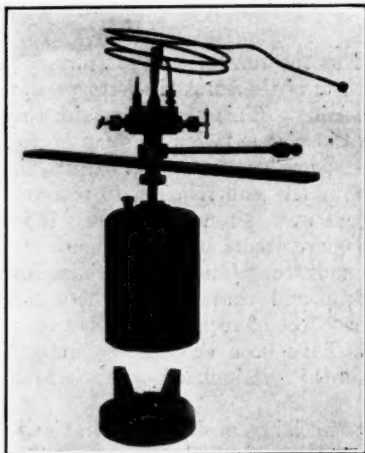

Figure 12A—Experimental Devulcanizer

cent of sulfur to the rubber produced no shifting of the peak but simply lowered the modulus curve. Figure 20 shows the effect of making a greater percentage reduction of sulfur in the highly compounded mixture VIII. Here the sulfur
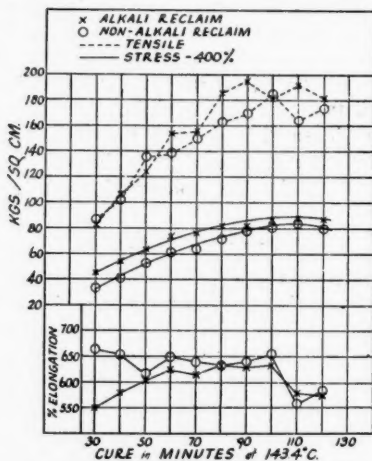

Figure 13—Effect of 10 Per Cent Alkali and Non-alkali Reclaims in Tread Compounds XIII and XIV

to rubber (new rubber plus rubber in reclaim) was reduced from a total sulfur (added sulfur plus total sulfur in the reclaim) of 3.58 per cent to a total sulfur of 2.70 per cent,

which is a reduction of 24 per cent. The new sulfur added in one case was 2.8 per cent to the rubber, in the other 1.8 per cent, or a reduction of 35.7 per cent. While this very low sulfur content resulted in accentuating the peak, owing to the rapid softening of the compound with over-cure, the optimum point appears at approximately the same time of cure (75 minutes) in both cases. The curve is so flat in the case of the higher sulfur mixture that there might be some question relative to the maximum, but the stress-at-break curve leaves little doubt as to the equivalence in rate of cure of these two mixtures.

The futility of attempting to reduce the rate of cure of a mixture containing reclaim by reducing accelerator is shown in Figure 21. The curves cover the data obtained on compound VIII, containing 0.97 per cent of di-*o*-tolylguanidine to the rubber, together with a mixture in which the accelerator content has been reduced to 0.45 per cent and another mixture from which all organic accelerator has been removed.

The result of this characteristic of retaining rate of cure regardless of sulfur or accelerator concentrations is that it is extremely difficult, in using reclaimed rubber, to balance the cure in the various parts of a thick article. For example, in a pneumatic tire the carcass must have a much faster curing rate than the tread, for the tread, especially on the outside, gets much more heat during vulcanization than the carcass. This is true even when the tire is cured "on water"—i. e., cured on a rubber bag filled with hot water—but it is true to an even greater extent where a tire is cured on "air," for the heat transfer through air is much slower.

From this it would appear that the use of reclaim in a carcass compound—i. e., the compound used in insulating the plies of fabric—would be advantageous, and this is the case from the

Figure 14—Effect of Added Alkali on Tread Compound XIV

standpoint of curing rate. On the other hand, when reclaim is added to a tread mixture the rate becomes so fast that in order to vulcanize the tread properly the temperature or duration of the curing period must be reduced to such an extent that it becomes difficult to cure the carcass properly. A remedy is, of course, to speed up the carcass
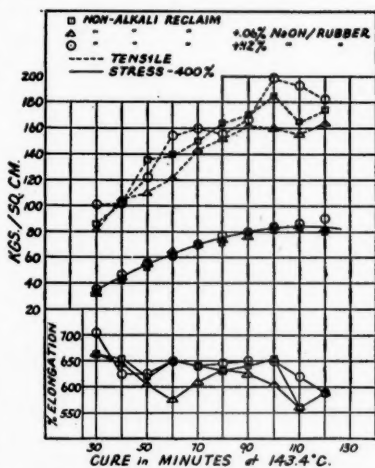
through the use of ultra-accelerators, but this makes it very difficult to process the fabric as the curing rate of the skim compound is such that premature vulcanization or "scorching" is liable to occur during the calendering operation, ruining the processed fabric.

As a result many tires on the market today containing reclaim are seriously overcured with respect to the tread. And this is not always incidental to the use of reclaim. It seems to be the practice of some to use a high-sulfur ratio in their recipes which have a high reclaim content in order to increase the tensile strength. A "full" cure always improves tensile properties whether a stock contains reclaim or not, but experience has, or should have, taught the rubber technologist to keep his products below the state of optimum properties when freshly cured, for otherwise they suffer distinctly after a period of aging. The temptation to use high sulfur in the case of compounds containing reclaimed
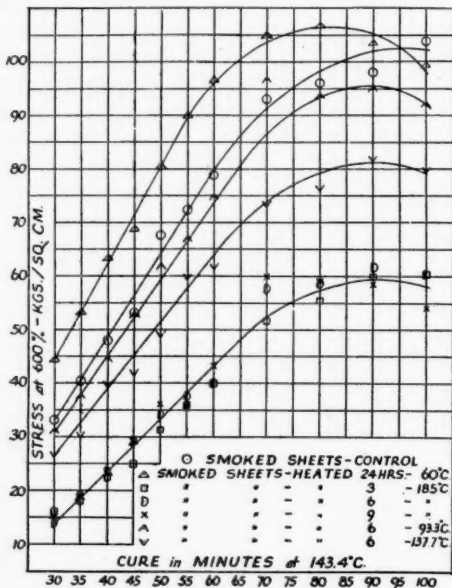

Figure 15—Effect of Heat-Treated Pale Crepe in Compound XV

rubber is great, for appreciable amounts of reclaim lower tensile strength and it is one of the technologist's problems to remedy this.

Of equal, if not greater, importance is the problem of maintaining the physical properties during aging. It has already been pointed out that the percentage of combined sulfur in reclaim is high. When this is used in compounding and undergoes a second vulcanization, the combined sulfur is still further increased. It has been shown[22] that the com-

[22] Shepard and Krall, *Ind. Eng. Chem.*, **14**, 951 (1922).

bined sulfur or chemical state of cure is no criterion of initial physical properties, but it is certain that no rubber technologist is unaware of the detrimental influence of high chemical state of cure on the aging properties of soft-rubber products. The trend toward low-sulfur, non-blooming compounds has been chiefly due to the better aging obtained with such compounds provided they are properly cured, and only secondarily to a desire to improve the appearance through eliminating the unsightly sulfur bloom from the surface.

To how great an extent the technologist's views on this question of the influence of chemical state of cure on the stability of rubber products have changed is shown in the following quotation from C. O. Weber:[4] "It is well recognized that the higher we vulcanize India-rubber—i. e., the
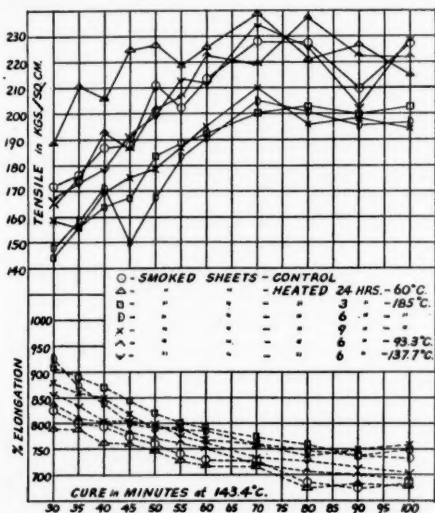

Figure 16—Effect of Heat-Treated Pale Crepe
in Compound XV

higher the proportion of combined sulfur it contains, the smaller is its liability to oxidize or deteriorate, generally speaking." It was his belief that this was a logical consequence of the reduction in unsaturation of the rubber molecule, but on this theory vulcanized rubber should be more stable than the unvulcanized product, which is not the case.

High combined sulfur being inevitable in reclaimed rubber as made at present, it is clear why the aging qualities of products containing reclaim cause much concern. The use of antioxidants has greatly assisted in improving the aging properties, but their effect is curative, not preventative. To get at the root of the trouble the cause must be removed, and in the writers' opinion one of the chief causes is the high chemical state of cure. Apparently Boiry[23] is of the

Rev. gén. caoutchouc, Spec. No. (Livre d'Or), 205 (January, 1927).

same opinion, for he recommends that reclaimed rubber should not be made from cured rubber with too high a coefficient of vulcanization.

Removal of the chemically combined sulfur in reclaim has never been accomplished without subjecting the rubber scrap to such deep-seated changes that the product is commercially valueless.[23,24] Present methods of alkali reclaiming are such that, though some of the free sulfur in the scrap may be removed by the alkali during the process, the combined sulfur is actually increased (Table II), probably because the high temperatures used combine a part of the free sulfur before it is removed by the alkali. Ways and means of preventing this become increasingly important as reclaimed rubber is "re-reclaimed." In order to prove whether reduction of the combined sulfur in reclaim really does mean anything from an aging 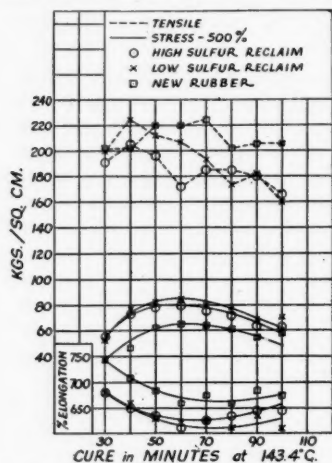standpoint, experiments were carried out using tread compound X cured 90 minutes at 143.4° C. as scrap for reclaiming. The results are shown in Table II.

Figure 17—Effect of 25 Per Cent of High- and Low-Sulfur Reclaim on Pure-Gum Compound XVIII

Table II—Effect of Reclaiming on Combined-Sulfur Content

	FREE SULFUR	TRUE COMBINED SULFUR[25]	TOTAL SULFUR
	Per cent	Per cent	Per cent
Original scrap	0.64	0.93	1.68
Water cook	0.13	1.31	1.73
8% caustic cook	0.14	1.16	1.67

It is clear from these figures that, while the alkali was more effective than the water in keeping down the combined sulfur, the value rose in both cases, the increase, even in the case of the alkali cook, amounting to 24.7 per cent.

Table III—Effect of Pretreatment on Combined-Sulfur Content of Reclaim

	FREE SULFUR	TRUE COMBINED SULFUR	TOTAL SULFUR
	Per cent	Per cent	Per cent
Without pretreatment at 60° C.	0.19	1.82	3.07
With pretreatment at 60° C.	0.18	1.29	2.45

In an effort to bring about a reduction instead of an increase in combined sulfur, a sample of well-blended whole-tire scrap was treated with 8 per cent caustic at 55–65° C.

[24] Alexander, *Chem.-Ztg.*, **36**, 1289, 1340, 1358 (1912).
[25] Kelly, *Ind. Eng. Chem.*, **14**, 196 (1922).

for 60 hours to remove free sulfur; at the end of this pretreatment the alkaline liquor was decanted and the scrap thoroughly washed. It was then devulcanized according to the usual procedure, using 8 per cent caustic for 9 hours at 183–184° C. As a control another sample of the same scrap was devulcanized without this pretreatment. The analytical results on these two samples are given in Table III.
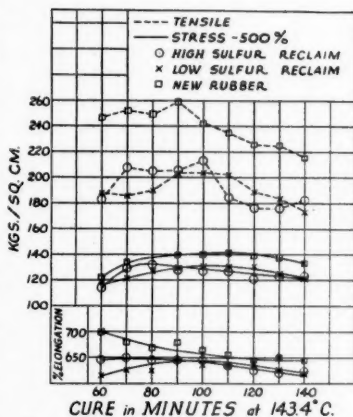

Figure 18—Effect of 18 Per Cent of High- and Low-Sulfur Reclaim on Tread Compound XIX

The result of this pretreatment was thus a *reduction* in combined sulfur of 29.1 per cent. These two reclaims were then used in compounding tread XX in which the reclaimed rubber amounts to 20 per cent.

	XX
Smoked sheets	48
Amber crepe	39
Rolled brown crepe	13
Reclaim	45.5
Sulfur	3.3
Di-o-tolylguanidine	0.9
Zinc oxide	15.5
Gas black	56
Pine tar	6.8
	228.0

Table IV shows the physical properties of the resulting compounds when cured for 80 minutes at 143.4° C. (best aging cure), both when freshly cured and when aged in the dark for 1 year, artificially aged for 8 days at 70° C., and for 27 and 36 hours, respectively, in the oxygen bomb at 60° C. (300 lbs. pressure of oxygen). Heat aging for 8 days

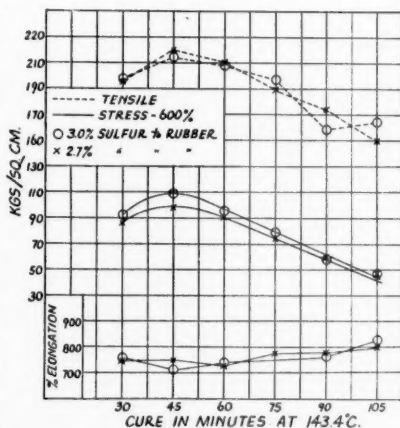

Figure 19—Effect of Reducing Sulfur Concentration in Compound II

at 70° C. failed to differentiate appreciably these stocks, while oxygen-bomb aging for long periods showed up definite differences in favor of the compound containing the reclaim

Table IV—Tensile Strength of Tread Compound XX, Cured for 80 Minutes at 143.4° C.

True Combined Sulfur Content of Reclaim	Freshly Cured	1 Year Natural Aging		8 Days at 70° C.		In Oxygen Bomb			
						27 Hours at 60° C.		36 Hours at 60° C.	
		Actual	Change	Actual	Change	Actual	Change	Actual	Change
Per cent	Kg./sq. cm.	Kg./sq. cm.	Per cent	Kg./sq. cm.	Per cent	Kg./sq. cm.	Per cent	Kg./sq. cm.	Per cent
1.28	191	135	−29.3	139	−27.2	112	−41.3	99	−48.2
1.52	185	126	−31.9	136	−26.5	90	−51.3	88	−52.4

of lower combined-sulfur content. While this lost 41.3 per
cent in tensile strength, the compound containing the re-
claim of higher combined sulfur lost 51.3 per cent; the loss
of the latter was thus 24.4 per cent greater than that of the
former. After 36 hours' aging in the oxygen bomb the
difference was 8.7 per cent. Natural aging brought out a
difference in percentage deterioration of 8.9 per cent. These
figures point definitely to the superiority of the reclaim of
lower combined sulfur, and indicate clearly one of the prob-
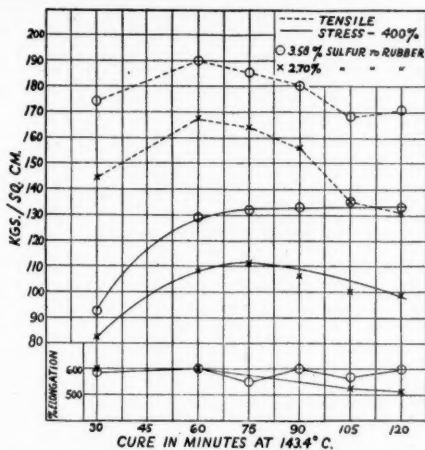lems before the reclaimer in making a reclaim from scrap

Figure 20—Effect of Reducing the Sulfur Con-
centration in Compound VIII

containing a high percentage of reclaimed rubber. In the
light of the above findings, the views of Weber[4] are subject
to question:

The decrease in the state of non-saturation of the India rubber
in a soft rubber article remains intact in the subsequent recovery
process, and on revulcanizing this recovered rubber the unavoid-
able result is that the state of non-saturation is still further
reduced. The effect of this, as a matter of course, is to greatly
increase the stability of the revulcanized recovered rubber.

The writers are at present studying this problem, and through
the use of the experimental devulcanizer described in this
paper expect to be in a position to publish on this in the
near future.

Summary and Conclusions

The rapid rate of cure of reclaimed rubber, while un-
doubtedly influenced by the alkali used in the reclaiming
process, is only partially attributable to the presence or
influence of alkali. Not only is this clearly shown by the
experimental data, but by the fact that reclaimed rubber
prepared in the absence of alkali, though slower curing, is
still much faster in curing rate than new rubber.

In spite of the plausibility of the theory that depolymeri-
zation or disaggregation under the influence of heat and
mechanical working is responsible for the rapid rate, the

48

experimental data obtained by subjecting new rubber to devulcanization temperatures do not support this.

From the data presented it appears that the chemically combined sulfur in reclaim is not an important factor in the rate of cure. This point is being further investigated, as is also the influence of residual accelerator, and of oxidation products.

'While the amount of combined sulfur in reclaimed rubber appears to have little to do with the rate of cure, its influence on the aging qualities of compounds containing reclaim is pronounced, reduction in the combined sulfur leading to better aging. Consequently the problem of true devulcanization in a chemical sense is one warranting renewed interest.

As a result of this study of reclaimed rubber, the writers are led to the conclusion that in compounding with reclaimed rubber it is highly desirable, and quite necessary from an aging standpoint, to use a low concentration of sulfur, and to reduce either the time or temperature of vulcanization.

Acknowledgment

The authors are indebted to Harry L. Morris, of this laboratory, for his valuable assistance in connection with the compounding data presented in this paper.

Discussion

Q. By what method was alkalinity determined, how was sodium hydroxide determined, and was the water used free from alkali?

A. Distilled water was used both in the devulcanization experiments and in the alkalinity determinations. This water was neutral, as determined by ordinary indicators.

The method of determining alkalinity was as follows:

The sample was sheeted to 0.005 inch thickness, and 100 grams of this were boiled vigorously in distilled water for 3 hours, thereupon removed, the adhering liquid squeezed out by hand (the operator using rubber gloves free of any trace of alkali), and the sample given four rinsings and squeezings with hot distilled water. Thereupon the sample was redigested for 2 hours, the rinsing process being repeated. All the extraction liquors were combined and titrated to neutrality with N sulfuric acid using methyl red as indicator. The total alkalinity is given as per cent NaOH.
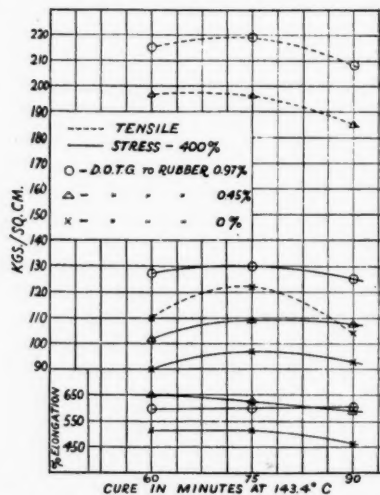
Figure 21—Effect of Reducing Accelerator Concentration in Compound VIII

Q. It has been found that by very long extractions, up to

as high as 48 hours, the alkali content increases up to 0.5–1 per cent. The question is whether all alkalinity was determined as above.

A.   We have found that in two subsequent digestions very small amounts of alkaline material were further extractable—about 0.002 to 0.004 per cent per digestion. The method used is satisfactory for comparative tests. Assuming that further small amounts of alkali were present, however, the data presented are all the more conclusive that residual alkali accounts in only a small measure for the rapid rate of cure of reclaimed rubber.

Value of the Rubber Hydrocarbon in Reclaimed Rubber

W. W. Vogt

THE GOODYEAR TIRE & RUBBER COMPANY, AKRON, OHIO

**Tire-tread stocks containing reclaim were so compounded
that their ultimate composition was the same except for the
percentage of reclaimed-rubber hydrocarbon substituted
for new-rubber hydrocarbon.   Cures were adjusted to give
the technical optimum in the same time of cure.   The
cured stocks were subjected to tensile and abrasion tests by
five methods.   The results show that the value of the re-
claimed-rubber hydrocarbon varies from zero, when sub-
stituted in small percentages, up to a maximum of 50 per
cent of the value of new rubber, when compounded in
large percentages.**

I N ORDER to determine the value of the hydrocarbon
present in reclaimed rubber compared with that in new
rubber, it is necessary to compound the stocks in such
manner that the percentage and kind of fillers, softeners,
etc., are constant, the only variable being the percentage of
the total rubber hydrocarbon which has been introduced in
the form of reclaimed hydrocarbon.   It is also necessary to
adjust curing ratios in such fashion as to compensate for the
accelerating or activating effects of the reclaim, so that all
stocks reach technical best cure in the same length of curing
time.

Experimental

COMPOSITION AND PROPERTIES OF RECLAIM—The reclaim
used was a typical high-grade, alkali-process, whole-tire
reclaim having the following characteristics:

Per cent

Acetone extract	10.4
Total sulfur	3.0
Free sulfur	0.08
Free carbon	7.5
Ash	19.3 (ZnO, 10.5, insoluble, 8.8)
Specific gravity	1.23

When cured in a formula consisting of 100 parts reclaim and 5 parts sulfur for 18 minutes at 2.8 kg. per sq. cm. (40 pounds) steam pressure (141.5° C.), it gave a tensile of 55 kg. per sq. cm. (800 lbs./sq. in.) and an elongation of 450 per cent.

The insoluble matter was assumed to be 50 per cent clay and 50 per cent barytes. The acetone extract was assumed to be 50 per cent mineral rubber and 50 per cent thin pine tar. The hydrocarbon content of the reclaim was figured at 55 per cent.

Note—These assumptions are in line with general experience with this type of reclaim. Furthermore, the exact ratio of clay to barytes makes very little difference in the ultimate physical properties of the compounds inasmuch as neither contributes any marked qualities to the final rubber compounds. The same may be said of the acetone extract. Outside of effects on the rate of cure, which have been compensated for in another manner, the type of softener assumed is unimportant. The rather high percentage of pine tar assumed was based on the knowledge that some of this material was used in the reclaiming process.

METHOD OF COMPOUNDING—The lowest grade compound was designed to contain 40 parts of new rubber hydrocarbon and 60 parts of reclaimed hydrocarbon and therefore the rubber base would be 40 of new rubber and 108 of reclaim (= 60 of hydrocarbon). As a result 108 parts of reclaim would contain:

108×10.4 per cent = 11.2 parts acetone extract (5.6 mineral rubber, 5.6 thin pine tar)
108×7.5 per cent = 8.1 parts carbon black
108×10.5 per cent = 11.3 parts ZnO
108×8.8 per cent = 9.5 parts insoluble (4.8 clay, 4.7 barytes)

Hence, these quantities of the various fillers and softeners will be unavoidably introduced in the lowest grade compound. The base compound containing all new rubber must then be made to contain these additions, in order to secure constancy of composition over the series.

It was known that the accelerating or activating effect of the reclaim could be duplicated by adding a small amount of litharge to the new-rubber base stock, so 0.5 part of the rubber was added to the base stock and this amount decreased in successive formulas as reclaim was added. This expedient gives a practically uniform rate of cure throughout the series The complete formulas are given in Table I.

These stocks were milled in about 4-kg. batches on a 50-cm. (20-inch) laboratory mill. The mineral rubber was added to the new rubber. The gas black and the accelerator were added in the form of a master batch. The new rubber containing the mineral rubber, the gas black master batch, and the separately broken-down reclaim were blended together and

the rest of the ingredients added to the batch. Further compounds were made up in the following manner: New batches of stocks 1, 6, and 7 were milled and with the excess stock of the remaining batches were combined in such proportions by weight as to duplicate the chemical composition of stocks 1 to 7 (Table II). By so doing it was thought that some light might be cast on the question as to whether the law of mixtures was obeyed.

Table I—Stock Formulas

Stock	1	2	3	4	5	6	7
% Reclaim hydrocarbon	0	5	10	20	30	45	60
Pale crepe	100	95.0	90.0	80.0	70.0	55.0	40.0
Reclaim	0	9.0	18.0	36.0	54.0	81.0	108.0
ZnO	16.5	15.5	14.6	12.7	10.8	8.0	5.0
Gas black	43.0	42.3	41.6	40.3	39.0	36.9	35.0
Clay	4.8	4.6	4.4	3.2	2.4	1.2	0.0
Barytes	4.7	4.5	4.3	3.1	2.3	1.1	0.0
Mineral rubber	5.6	5.1	4.6	3.7	2.8	1.4	0.0
Pine tar	5.6	5.1	4.6	3.7	2.8	1.4	0.0
Litharge	0.5	0.45	0.4	0.32	0.23	0.1	0.0
Stearic acid	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Sulfur	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Captax	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Total	189.2	190.05	191.0	191.52	192.83	194.6	196.5

The results of this series confirmed those of the first series so exactly that it was concluded that the law of mixtures holds.

Table II—Composition of Mixed Stocks

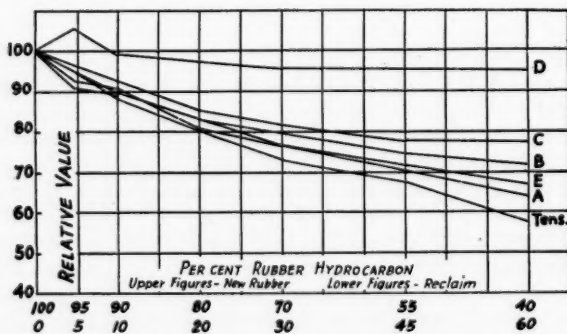| Stock	21	22	23	26	24	28	25	29	30
% Reclaim hydrocarbon	0	5	10	10	20	20	30	45	60
Stock									
1	1	1	1	2	2				
2									
3		1					1		
4			1						
5				1			1		
6								1	
7						1		1	1

Figure 1

Testing Procedure—Standard procedures for physical testing were followed throughout, with care to give all stocks similar treatment. A range of cure from 30 to 90 minutes at 126° C. (258° F.) was obtained and the tensiles were practically identical over this range for all stocks. Hence the

results on tensile are quite independent of cure. The abrasion results were obtained on the 60-minute cure for all stocks. This was judged to be the technical optimum.

All the data given are the average results secured from at least two, and in some cases three, batches of each stock, involving separate sets of cures. The tensile data are the average of all cures in the flat part of the curing curve, so that each point in Figure 1 represents at least two batches of four cures of three strips (two highest), or twenty-four separate tensile determinations. The abrasion data represent at least two batches of one cure of two test pieces on each type of machine. Since the conditions were so varied on the different types of abrasion machines, the data are presented in a comparative manner using stock 1 as a standard.

Tensile Strength and Other Physical Tests

The values for tensile strength for all the stocks are given in Table III.

Table III—Tensile Strength of Various Stocks

			Kilograms per square centimeter			
Per cent reclaim hydrocarbon	0	5	10	20	30	45	60
Per cent new-rubber hydrocarbon	100	95	90	80	70	55	40
Stocks	1	2	3	4	5	6	7
	21	22	23	24	25	29	30
			26	28			
Tensile	290	275	255	230	210	195	170
	280	270	255	230	220	200	175
			255	235			
Average tensile	285	272	255	232	215	197	172
Tensile as per cent of stock 1	100	95.5	89.5	81.5	75.5	69	60

The results are shown graphically in Figure 1, as is also the relative abrasion resistance by methods A to E as shown in Table V. Further data on the stress-strain properties of the best cure (60 minutes at 126° C.) of the stocks are given in Table IV, together with other data as to hardness, etc. The mechanical efficiency was obtained on small blocks of rubber by means of a pendulum rebound machine. At the same time the penetration of the pendulum hammer into the rubber was measured to 0.001 inch (0.025 mm.) and the reciprocal of this deflection is termed the "dynamic hardness."
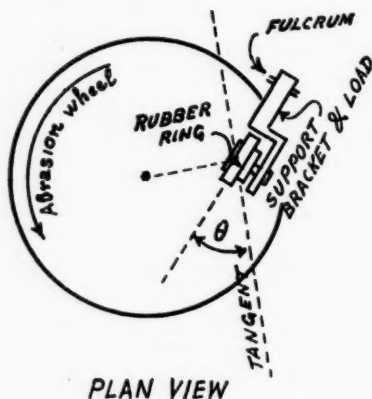
It will be noted that as the percentage of reclaim hydrocarbon is increased the modulus at the low elongation (200 per cent) increases, while at the high elongation (500 per cent) it decreases. This corresponds to a rotation of the stress-strain curves about a point of constant modulus (about 400 per cent). Stocks containing reclaim are stiffer than, equal to, or softer than the equivalent stock compounded from new rubber depending on which point of the stress-strain curve is used as a basis for comparison. In other words, reclaim stocks have a lower stiffness index figure according to Dinsmore or a higher type figure according to Schidrowitz. Both writers agree that either a lower stiffness index or a higher type means an inferior product.

Abrasion Results

All the methods, with the exception of that one using Williams' machine[1] (Grasselli abrader), made use of test specimens in the form of annular rings of the following dimensions: o. d., 87.5 mm. (3.5 inches); i. d., 50.0 mm. (2.0 inches); thickness, 17.5 mm. (0.68 inch). The periphery of the ring makes contact with the abrasive surface under suitable conditions of slip. The abrasive surface in all cases was a 36-grain alundum wheel.

METHOD A (Figure 2A)—The ring is set perpendicular to the abrasive surface and at an angle with respect to the tangent of the abrasive wheel which passes through the center of the area of contact of the rubber ring and the abrasive. The abrasive wheel is driven by the motor.

Conditions:

Angle (Θ)	16 degrees
Load applied on rubber ring	14.5 kg. (32 lbs.)
R. p. m. of abrasive wheel	80
Surface speed of abrasive wheel at center of area of contact with rubber ring	137 meters (450 feet) per minute
R. p. m. of rubber ring	About 500

PLAN VIEW

Figure 2A

METHOD B (Figure 2B) —An abrasive wheel is mounted coaxially with a heavy flywheel. The rubber ring is mounted on the shaft of a constant-speed motor, which is in turn mounted on a freely moving carriage. A weight is used to press the rubber ring against the periphery of the abrasive wheel. It will be appreciated that the flywheel system has a constant moment of inertia and that if the rotating rubber ring is placed in contact with the stationary abrasive wheel slippage, and consequently abrasion, will take place until the abrasive wheel is running at the same surface speed as the rubber ring. Furthermore, a definite amount of energy must be supplied to the flywheel system to bring it to this condition. As a result a certain amount of rubber will be abraded while a definite quantity of energy has been *transmitted through* the rubber ring to the flywheel system. The loss per cycle is taken as the unit of measurement. The principle of this machine was suggested by A. M. Hamblet.

Conditions:

R. p. m. of rubber ring	1780
R. p. m. of abrasive wheel	0 to 515
Surface speed of rubber ring	450 meters (1625 feet) per min
Surface speed of abrasive wheel	0 to 495 meters (0 to 1625 feet) per minute
Load applied	2.27 kg. (5 lbs.)

METHOD C (Figure 2C)—The same set-up is used as in method B. A tachometer is mounted on the flywheel shaft and when

[1] *Ind. Eng. Chem.*, **19**, 674 (1927).

Table IV—Physical Properties of Stocks

Stock	Reclaim Hydrocarbon %	Modulus—Kg. per sq. cm.				Av. Tensile Kg. per sq. cm.	Elongation %	Shore Hardness	Dynamic Hardness	Mechanical Efficiency %
		200%	300%	400%	500%					
1	0	47	85	135	198	285	625	70	4.38	63.1
2	5	51	88	140	195	272	600	71	4.62	64.2
3	10	48	85	132	190	255	595	72	4.80	60.0
4	20	52	86	134	186	232	580	71	5.02	57.0
5	30	52	88	132	182	215	560	71	5.02	56.5
6	45	57	93	134	178	197	540	72	5.02	58.5
7	60	57	93	131	172	172	500	71	4.95	59.0

the system is running at maximum speed a strap brake is applied to the flywheel to cut down its speed any given amount. Since the rubber ring is maintained at constant speed, a certain differential slip is set up and abrasion ensues. The test is continued for a given length of time, and from the value of loss so obtained is subtracted the loss due to one cycle (of method B).

The general conditions were the same as in method B. The slip was calculated as the reduction in r. p. m. of the abrasive wheel divided by the maximum r. p. m. of the abrasive wheel times 100. The value used in the present experiments was 30 per cent, corresponding to a surface slip of about 150 meters (500 feet) per minute.

METHOD D (Figure 2D)—The rotating rubber ring is pressed against the abrasive wheel, but the plane of the rubber ring makes an angle (Θ) with the plane of the abrasive wheel. This sets up a slippage with consequent abrasion.

Conditions:

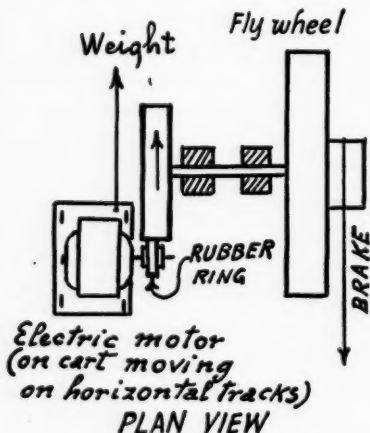|	
Angle (Θ)	20 degrees
Load on rubber ring	2.27 kg. (5 lbs.)
R. p. m. of rubber ring	1780
Surface speed of rubber ring	495 meters (1625 feet) per minute
Surface speed of abrasive whee	1625 $\times$ cos Θ = 465 meters (1530 feet) per minute
Maximum r. p. m. of abrasive wheel	485
Slip	1625 $\times$ sin Θ = 170 meters (555 feet) per minute

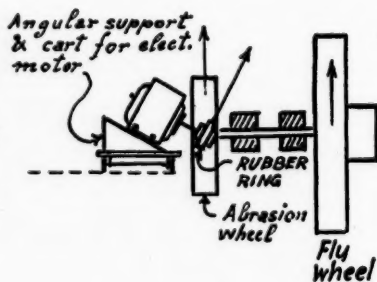
PLAN VIEW

Figure 2B & C

SIDE VIEW

Figure 2D

The test is conducted for a given length of time and no correction is made for the abrasion which takes place during the period in which the abrasive wheel is attaining its maximum speed.

METHOD E—The Grasselli abrader (Williams' machine) is used according to the standard conditions recommended by Williams:[1] load, 3.64 kg. (8 lbs.); time, 20 minutes.

The results are figured on the basis of cubic centimeters per horsepower-hour. All these methods gave duplicable results, and seldom was the maximum variation as much as 5 per cent. The mean variation was 2 to 3 per cent.

A summary of the averages of all stocks 1 to 7 and 21 to 30 by the various methods is given in Table V, wherein the values given are for abrasion resistance with the all new-rubber stock 1 assigned an arbitrary value of 100.

Values less than 100 indicate inferior wearing stocks. Method D gives results which show that all stocks are virtually the same. Since the only property which is approximately constant for all stocks is their hardness, it might be inferred that this method measures hardness almost exclusively. The other methods, particularly A and E, agree very well.

Table V—Abrasion Resistances (Figure 1)

| STOCK | NEW-RUBBER HYDRO-CARBON % | RE-CLAIM HYDRO-CARBON % | METHOD | | | | |
			A	B	C	D	E
1, 21	100	0	100	100	100	100	100
2, 22	95	5	93	95	96	106	91
3, 23, 26	90	10	91.0	90	92	99	89
4, 24, 28	80	20	81.0	83	85	97	83
5, 25	70	30	77.0	..	82	96	77
6, 29	55	45	71.0	75	77	95	72
7, 30	40	60	65.0	72	77	95	67

Interpretation of Results

Both the tensile and the abrasion-resistance figures indicate clearly that for additions up to 20 per cent of reclaim hydrocarbon no value is obtained from the reclaim hydrocarbon. Above this point the reclaim hydrocarbon shows a positive value. The following analysis is an attempt to evaluate the reclaim hydrocarbon in terms of new-rubber hydrocarbon:

Let A = value of abrasion resistance or tensile strength of new-rubber hydrocarbon, and let it be assigned a value of 100 units

B = value of reclaim hydrocarbon in the same units

C = experimentally determined values for abrasion resistance or tensile strength (based on new-rubber stock = 100) of various stocks

Y = amount of new-rubber hydrocarbon as a decimal fraction and $1.00 - Y$ = amount of reclaim hydrocarbon as a decimal fraction

Then $Ay + B (1.00 - y) = C$ on the assumption that the qualities of the two types of hydrocarbons are additive.

Solving for $B = \dfrac{C - Ay}{1.00 - y}$

The B value is the intercept on the vertical axis in Figure 1 at the 100 per cent reclaim point of a line drawn from the 100-unit point on the vertical axis through any experimental point on the various curves. Taking the values of C for tensile strength from Table III and the values for abrasion resistance from Table V and solving for B we get the figures given in Table VI.

These values apply to the particular methods of testing used and to the particular stocks employed, and since the value changes with the amount of reclaim hydrocarbon substituted for new-rubber hydrocarbon, it is not capable of general application. The method of evaluation might, however, be profitably extended to various types of compounds and to various methods of testing.

These results might be construed to mean that reclaim is worthless when used in small amounts in high-grade tread compounds. This is by no means a fact. They do mean,

however, that a method of compounding which substitutes reclaimed hydrocarbon for new-rubber hydrocarbon without other changes and adjustments in the formula may give adverse results.

Table VI—Values of Reclaim Hydrocarbon

NEW-RUBBER HYDRO-CARBON	RE-CLAIM HYDRO-CARBON	FROM TENSILE STRENGTH	FROM ABRASION RESISTANCE BY METHODS				
%	%		A	B	C	D	E
100	0	..	..	..	..	..	..
95	5	0	Neg.	0	20	220 (?)	Neg.
90	10	Neg.	1	0	20	90	Neg.
80	20	0	5	15	25	85	15
70	30	10	23	..	40	86	23
55	45	27	35	45	49	89	38
40	60	30	42	33	62	92	37

Holt and Wormeley[2] published results of road tests and laboratory abrasion tests on tire treads containing reclaim. The writer has recalculated the composition of the compounds listed by them (page 580) on the same basis as used in the present paper and on the assumption that the reclaim used had the same analysis as that used here. Table VII gives some comparisons.

In spite of the fact that the substitution of new-rubber hydrocarbon by reclaimed-rubber hydrocarbon is accompanied by an increase in the percentage of carbon black (the main reënforcing pigment), the wear resistance drops off faster than the percentage of new-rubber hydrocarbon, thus giving negative values for the reclaim hydrocarbon. These results confirm in the main the conclusions of the present paper.

Table VII—Comparison of Laboratory and Road Tests

Stock	1A	1B	1C	1D
Per cent new-rubber hydrocarbon	100	90.4	82.7	76
Per cent reclaim hydrocarbon	0	9.6	17.3	24
Parts carbon black per 100 total hydrocarbon	26.2	28.2	30.0	31.2
Parts ZnO per 100 total hydrocarbon	20.5	21.4	18.0	15.5
Road-wear index	100	85	80	73
B value		Neg.	Neg.	Neg.

Acknowledgment

The writer wishes to express his appreciation to R. P. Dinsmore for valuable suggestions and criticism.

[2] *Bur. Standards, Tech. Paper* **294.**

Factors in Processing Reclaimed Rubber

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Production of reclaimed rubber of uniformly good
physical and chemical properties is dependent first upon
judicious classification and blending of raw materials.
Grinding to a state in which no large particles are present,
but without an excess of fines, allows a minimum de-
vulcanizing time at a given temperature, decreases the
tendency to depolymerize to an objectionable extent, and
reduces the requirement for softeners.   These conditions
facilitate further processing to a smooth product of good
quality with the desired plasticity and with optimum
compounding, milling, calendering, and tubing char-
acteristics.   Devulcanization at high temperatures tends
to reduce the tensile slightly and to increase the elonga-
tion as compared with treatment at lower temperatures.
Alkali reclaims require efficient washing to remove residual
caustic and the recovery of fines from the wash liquors
involves problems of settling and filtration or screening.
Drying of wet-processed reclaims at high temperatures
or for an excessively long time results in tacky products,
just as does over-devulcanization.   A minimum amount
of milling and refining at normal temperatures is desirable
to preserve the quality, therefore previous processing
should be thorough and uniform.

Some comparisons of types of equipment are made and
some desirable future developments are discussed.

IN ANY discussion of the factors especially influencing
the manufacture of reclaimed rubber with optimum
physical and chemical properties there naturally arises
first the problem of the proper classification, selection, and

blending of the scrap rubber. Reclaimers are appreciating more every day the necessity of studying the nature of the materials from which they expect to obtain rubber substitutes of marketable value. The aim in blending scrap tires and parts of them, for instance, is not merely that of assuring the manufacturer that his tire reclaim will have a specific gravity within certain specified limits. The more important consideration is that of assembling materials which will respond reasonably alike to similar processing and which will give a uniform product of the best possible quality for a definite use. It is not enough to segregate the cheaper grades of scrap from the better ones. Even similar raw materials of approximately the same original quality vary greatly in their physical and chemical state owing to age, treatment while in use, and in the case of tires especially, account should be taken of the evident deterioration from overheating, oxidation, and exposure to sunlight. The reclaimer must also allow for great variations in the toughness, the proportion of rubber, and state of cure of the vulcanized materials.

Grinding

In rubber-reclaiming processes the preparation of raw materials has certainly as important an influence upon succeeding treatments and the ultimate character of the product as it exerts in most manufacturing operations requiring grinding and sizing. It is desirable to reduce vulcanized scrap to a certain maximum particle size and yet not to produce an excessive proportion of fines. If considerable oversize is present, the time of devulcanization and the extent of milling and refining must be increased in order to reduce these large particles to the proper state. In that case there is a tendency for an abnormal depolymerization of the finer particles and the final product is inclined to be tacky. So, under such unfavorable conditions, it is possible for a reclaim to be soft and tacky and yet contain comparatively hard lumps of unreduced material. Therefore, proper maximum particle size and reasonable uniformity are criteria of successful preparation.

In conjunction with this operation the removal of tramp metals presents a constant problem. Steel and iron are fairly well removed at this stage by magnetic separators, preferably the type which picks up these metals from a belt conveyor rather than the old pulley style of separator.

Grinding devices of several designs are in use. For such materials as scrap tires, inner tubes, solid tires, air bags, and certain classes of mechanical goods, the first step in reduction is accomplished with heavy roll crackers, or with a sturdy type of rag cutter or with hogs. The succeeding operation may be the passage through only one or a series of crackers or through a fine grinding hog or a shredder. Usually continuous screening is necessary to obtain the best

conditions. Following the first cutting or chopping opera-
tion, units consisting of a single cracker and a screen with
a continuous return of oversize to the cracker give very
good results. Choice of grinding equipment should be
based not only upon mechanical and production efficiencies
and upon the requirements previously pointed out, but
also upon an appreciation of the advantages of subjecting
most scrap rubber to a crushing action in order to facilitate
the succeeding treatments.

**Power Requirements for Grinding Representative Scrap Vulcanized
Materials under a Particular Set of Conditions**

MATERIAL	FINISHED RECLAIM Kilowatt-hours per lb.
Debeaded black tires	0.11
Inner tubes	0.19
Solid tires, air bags, etc. (high gravity)	0.16

In preparing vulcanized scrap containing cotton fabric
it is frequently suggested that the fiber be removed in the
course of the grinding operation so that there will conse-
quently be required a proportionately less quantity of
caustic soda in the devulcanizing process. So far no means
have been found for effecting a complete separation; fine
particles of rubber adhere to the disintegrated fabric, with
the result that too much rubber is lost and the value of the
fiber itself is lessened. The impure fiber is worth less than
linters and it cannot stand the cost of recovery. Neither
will the saving in caustic justify the expense of complete
separation.

Devulcanization

The so-called devulcanization of cured scrap rubber is the
most important step of the reclaiming process. It challenges
the interest of the chemist and the engineer and is the field
whence the principal future developments must come if there
is to be any great improvement in the properties of reclaimed
rubber. Several methods are employed dependent upon
the nature of the raw material.

FABRIC-FREE MATERIALS—*Direct Steam Heater and Pan Proc-
ess.* This method is popular in devulcanizing scrap inner
tubes, solid tires, air bags, and similar materials, especially when
it is not deemed necessary to remove the free sulfur by digestion
in caustic soda solution. Usually the ground scrap is first mixed
with softening agents and is then loaded into steel boxes. These
are stacked on cars with covers over each container or over the
top of the stacks, and the charge is run into a cylindrical heater,
similar to an inner-tube vulcanizer. The treatment consists in
heating the charge directly with live steam usually under pres-
sures of from 75 to 125 pounds. The heating period will vary
from 8 to 30 hours according to the character of the material.
The softened stock is then milled and refined.

Heater Process with Agitation. Sometimes it is desired to re-
move the free sulfur from fabric-free scrap and then to follow with
the heater method. In that case the ground scrap is digested for
several hours at atmospheric pressure in a hot solution of caustic
soda. It is then washed, partially dewatered, and charged into a
jacketed heater (usually horizontal) provided with an agitator.

Most of the residual moisture is driven off and devulcanization is then obtained under pressure by indirect heating. The finished charge is ready for milling and refining. The same type of devulcanizer may, of course, be employed when desulfurizing is not practiced.

This fabric-free class of scrap may also be simultaneously desulfurized and devulcanized by the alkali process and considerable tube reclaim is still made in that manner.

The Alkali Process—Devulcanization of cured rubber materials containing cotton fabric, such as pneumatic tires, is accomplished by subjecting them to high temperatures in caustic soda solution in steam-heated digesters—the well-known alkali process.

Two types of digesters or devulcanizers are in use, the vertical and the horizontal. These machines are jacketed for heating the contents indirectly by high-pressure steam. Agitators mix the charges of materials during the treatment. Certain advantages are claimed for both designs of devulcanizers. The vertical machines require barely half the floor space occupied by the horizontal devulcanizers of equal operating capacity. It is easier to obtain more efficient mixing in the horizontal type, since the action of the agitators carries upward the heavier particles of the contents which tend to settle to the bottom and the floating material is continuously swept down into the bulk of the charge. However, with efficiently designed agitators and proper speeds a homogeneous mixing is obtainable in either case.

The size of the charge must be proportioned with the view of insuring the best agitating and heating effects. The average charge for a 2000-gallon vertical devulcanizer is about 3500 pounds of ground scrap tires and 1100 gallons of caustic solution. The horizontal machines are usually 6 feet in diameter and have a capacity of approximately 3000 gallons; they take charges of about 5000 pounds of similar material and 1600 to 1800 gallons of caustic solution.

The ground scrap with the necessary quantity of caustic soda solution is charged into a digester, softeners are added, if desired, and the mixture is heated for a specified time. The proper treatment in the devulcanizing operation results in the conversion of the cotton fiber to soluble hydrocellulose, the removal of nearly all the free sulfur, and the plasticizing of the rubber. The first effect of the high temperature is to cause a small amount of the original free sulfur to combine with the rubber; in other words, there is an incipient vulcanization at the start of the process of devulcanization.

Typical Conditions in Reclaiming Debeaded Black Tires

STEAM PRESSURE	APPROX. TEMPERATURE	HEATING TIME	NaOH PER 100 LBS. SCRAP
Lbs.	*° F.*	*Hours*	*Lbs.*
125	353	24 to 36	130 to 140
150	366	14 to 20	130 to 135
195 to 200	385 to 388	8 to 14	125 to 130

The strength of the caustic solution will vary from 4 per cent to 6 per cent; the higher the temperature employed, the lower the caustic strength required. Destruction of the fabric is effected in 7 to 8 hours from the beginning of the heating period when the highest temperature is used, in 10 to 14 hours with 150 pounds steam, and in 18 to 24 hours with 125 pounds steam. If softeners are added, the plasticizing time, and, therefore, the total time, is usually in the lower range given in the table.

In devulcanizers of the types described containing approximately the charges mentioned and heated with steam at 195 to 200 pounds pressure, about $1^1/_2$ hours are required to raise the temperature of the contents to 350° F. and it is nearly 4 hours before a temperature near that of the jacket steam is reached.

Comparative steam requirements for devulcanization of the classes of scrap in question by the various methods are shown in the following table:

Steam for Devulcanization

MATERIAL	PROCESS	LBS. STEAM PER LB. FINISHED PRODUCT
Black tires	Alkali	1.40
Inner tubes	Heater (either type)	0.80
Solid tires, air-bags, etc.	Heater and pan	0.70

L. E. Weber[1] considers devulcanization as fundamentally a process of depolymerization and suggests that, if vulcanization is a polymerization, then the step in reclaiming cured rubber called "devulcanization" is properly termed, since it is to a large extent a reversal of the changes which occur in vulcanization. However, the theory has been advanced that physical disintegration rather than depolymerization may be the chief factor involved. Maximoff[2] holds that the mechanical plasticizing of raw rubber is one of mechanical disintegration rather than of depolymerization. Since plasticizing is an essential effect of devulcanization, it might be inferred that the devulcanizing process is just an extension of the breaking-down process, purely physical and not involving depolymerization. But it is pointed out that devulcanization imparts plasticity to a material lacking that property and that it is not a modification or continuation of an existing property. Maximoff assumes that the plasticizing of raw rubber is a result of the solution of the solid phase in the liquid phase and that devulcanization of cured rubber represents changes in the insoluble solid phase which is unstable at high temperatures. It is generally accepted that the principal effect of the heat treatments which we have reviewed is that of depolymerization.

Winkelmann,[3] Boiry,[4] and others have called attention to the deteriorating action of high temperatures incident to the present reclaiming methods and have advanced opinions on the mechanism of devulcanization. The connection between the amount and nature of the chloroform extract from acetone-extracted reclaimed rubber and the extent of its devulcanization seems to throw some light on the question. At least it appears that the chloroform extractable constituents are a measure of depolymerization or disaggregation and of plasticity. The extremely low viscosity of the chloroform extract is mentioned as evidence that it is composed of hydrocarbons in a low state of polymerization. Prolonged heating in devulcanization at the temperatures employed increases the chloroform extract while the acetone extract and the sulfur in the former change unnoticeably.

Devulcanization to the same apparent state of smoothness of the finished product at higher temperatures gives a

[1] "The Chemistry of Rubber Manufacture," p. 263.
[2] *Caoutchouc & gutta-percha*, **24**, 13,582 (1927).
[3] *Ind. Eng. Chem.*, **18**, 1165 (1926).
[4] *Rev. gén. caoutchouc*, Spec. No., 205 (January, 1927).

reclaim with slightly lower tensile and a little higher elongation than that obtained at lower temperatures.

With continued heating at the temperatures necessary in present methods the effect of depolymerization is also evidenced by an increase in plasticity and tackiness. Whitby[s] gives some of his own observations and comments upon the findings of Fickendey, Corter, Henri, Bernstein, and Van Rossem on the subject of tackiness of raw rubber. It is concluded that depolymerization or disaggregation is the fundamental cause but that the presence of oxygen is essential, that it has a catalytic influence on the depolymerization, and that the latter would not occur appreciably in its absence.

In devulcanizing cured rubber there are usually employed softening agents such as pine tars or pine oils, coal tar or pitch, mineral oils, asphalt-base softeners, etc. The tendency is to reduce the proportion of such agents and to eliminate their use entirely. If too much dependence is put upon their action for the purpose of assisting in making a "smooth" reclaim, the incorporation of the product in rubber compounds will give stocks that are troublesome in milling, calendering, and tubing operations. Since certain softeners promote good aging characteristics while others exert a deteriorating influence, their value should be gaged even more from these considerations than from their effects as plasticizers.

Washing Alkali Reclaims

The liquors in a finished charge from a devulcanizer, in which scrap tires, for example, have been treated by the alkali process, in addition to other varying constituents in solution or in suspension, contain sulfides and polysulfides and a certain amount of residual caustic soda which must be removed by washing. The soluble sulfur compounds are objectionable and it is well known that caustic in appreciable amounts renders the reclaim a dangerous material in a rubber stock owing to its action as an accelerator of vulcanization. A safe condition is a relative maximum content of 0.10 per cent sodium hydroxide as indicated by titration of a 4-hour boiling water extract of a 10-gram sample. The actual total alkalinity is determined by titration of no less than a 48-hour water extract. With continued extraction with hot water whole-tire reclaim may show a total alkalinity of 0.5 to 0.75 per cent where the ordinary test as reported in analyses may still be under 0.1 per cent.

When the caustic content of the liquors is appreciable— over 0.5 per cent NaOH, for instance—it is usually profitable to recover them and to use them as the base for fresh solutions for succeeding charges. In these cases the recovery of the weak solution is necessarily only partial and is effected by screening the entire contents of the devulcanizers. In systems using 195 to 200 pounds of steam the liquors normally contain about 0.5 per cent of sodium hydroxide and with

[s] "Plantation Rubber and the Testing of Rubber," p. 100.

pressures of 125 to 150 pounds the caustic content is about 0.7 to 1.0 per cent.

Various methods of washing the devulcanized materials are in vogue. In some instances it is flushed into large tanks and alternately washed and drained. Continuous screens and stationary, inclined screens are common. The continuous rotary washer performs this operation very successfully in several plants. It is simple, efficient, and requires little attention.

Efficient washing to a degree such that the finished reclaim will show an apparent alkalinity content below 0.10 per cent usually requires about $2^1/_4$ gallons of water per pound of product.
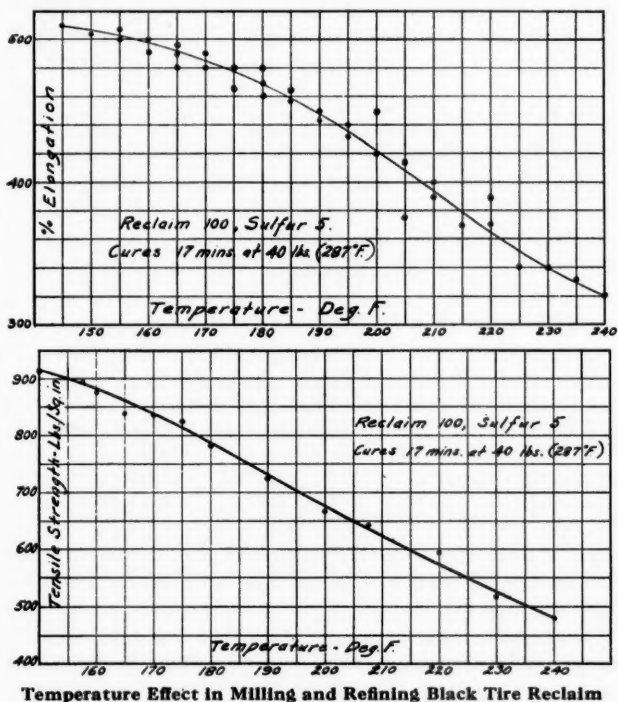
Temperature Effect in Milling and Refining Black Tire Reclaim

Previous to the washing operation it is often the practice to remove as much as possible of the non-magnetic tramp metal and such other foreign matter as small rock particles in "jigs" or on riffle tables. The presence of such impurities interferes with refining as well as being objectionable in the finished product.

RECOVERY OF FINES FROM WASH WATERS—The recovery of the fine devulcanized rubber from the wash waters presents another interesting chemical engineering problem. For every 1000 pounds of devulcanized material there is as much as 1500 gallons of this water with a content of about

1.0 per cent by weight of solids. In some cases the entire volume of wash water is sent direct to save-all screens, but lately there have been applied the settling and filtration principles frequently met in the general chemical industry. Continuous thickeners function well in the first step of concentration. About 85 per cent of the solids are easily settled and the remainder will float owing to the presence of air bubbles. The floating stock is skimmed off and added to the main sludge pumped from the bottom of the thickener.

The sludge mixture will normally contain 6 to 8 per cent of solid material. This is usually recovered either with continuous screens or with continuous rotary filters. An efficient filtering device will discharge the solids with 60 to 65 per cent moisture. The recovered material is added to the main bulk of stock just previous to the drying operation.

Dewatering

In the alkali process partial dewatering is done by continuous screw presses or centrifugals. The material delivered to the equipment may have a water content as high as 85 per cent. Efficient screw presses will reduce the water to 30 to 35 per cent. The Elmore continuous centrifugal has had several notable applications and a uniform discharge with 30 per cent of moisture is obtained. The power required for this operation averages 0.009 kilowatt-hour per pound of moisture-free material.

Drying

Drying previous to milling and refining is an important feature of the reclaiming process in its influence upon the characteristics of the final product. Though in the first stages the material may be subjected to somewhat higher temperatures, the final drying temperature should not be over 300° F., and preferably lower. High temperatures will cause depolymerization here also and the invariable result will be a tacky reclaim. If the moisture content is left too high, there is required an excessive milling and refining with a consequent lowering of the desirable qualities. Neither should it be completely dried. A maximum of 8 per cent and a minimum of 5 per cent is ordinarily the preferable range of residual moisture.

In some instances two-stage drying in oil- or gas-fired, direct-heat rotary driers is employed. The flow of material is countercurrent to the hot gases and a comparatively low temperature is maintained in the second stage. In another method the wet material is automatically spread in a thick layer over inclined screens through which heated air is passed. Continuous driers using air heated by steam coils are very efficient and have the advantage of insuring safe and uniform conditions. In this type of drier the initial temperature of the air at the wet end may be as high as 280° F. and the final incoming temperature as low as 150° F.

Milling and Refining

Milling and refining are necessary to break up any hard lumps of rubber and to plasticize the reclaimed product to a smooth condition in order to make it suitable for use in rubber compounds. Rubber reclaimed by the direct-steam heater method receives the same general treatment as does alkali reclaim, though usually less milling is required chiefly on account of its low moisture content.

Sixty- or 84-inch standard rubber mills are almost exclusively employed. They are often equipped with aprons which continuously return the material to the bite of the rolls, while in some cases the mills are provided with scrapper devices.

After mastication on mills the material is passed through a rough refiner (or breaker) as many times as are necessary and finally through a finishing refiner. The most modern type of machines has rolls with 30-inch faces, the front roll being about 24 inches in diameter and the back one 19 inches in diameter. Typical surface speed conditions are about 177 and 70 feet per minute, respectively. The action of this speed differential, combined with the fact that for many materials the rolls of the first refiners are set at about 0.01-inch gage and those of the finishing machines at about 0.005-inch, account for the term applied to the machines and the operation. The output from a finishing refiner will vary from 150 to 500 pounds an hour depending upon the character of the material.

Power Required for Milling and Refining

Reclaim	Kilowatt-hour per lb.
Black tires	0.45
Inner tube	0.265
Solid tire, air-bag, etc.	0.165

It is known that long milling and refining on cold machines greatly increases the plasticity of reclaimed rubber—just as it does raw rubber. It is also true that the qualities of reclaim are unfavorably affected by processing on abnormally hot mills and refiners. Temperatures over 200° F. are dangerous in most cases, grainy reclaim with decreased tensile and elongation resulting from overheating. Mill temperatures of 140° to 160° F. are preferable and the best refining temperature is usually from 165° to 185° F.

The effect of temperatures in milling and refining is illustrated by the accompanying curves. The temperatures indicated are those of the mill and refiner roll surfaces. The reclaim on the mills runs a few degrees hotter than the "working" rolls, but in every case the thin stock from refiners has a temperature very close to that of the front refiner roll.

Straining

Straining (followed by sheeting into slabs of convenient size) is ordinarily the final operation and is always necessary

in finishing tire reclaim in order to remove small pieces of metal and other foreign matter. Screw-type "strainers" with 26- to 30-mesh screens are used as a rule, though finer screening is practiced in some special cases. There is danger of overheating the reclaim when it is forced through very small openings. Here again temperatures must be controlled in order to preserve the quality of the product.

Note—No attempt has been made to discuss the "acid" process, since it is now applied to only a limited class of vulcanized scrap such as rubber footwear with a low sulfur content and to uncured fabric-containing scrap such as tire carcass trimming. However, for similar operations the same factors are at influence as in the alkali and the heater processes.

Future Developments

The comment is frequently made that there have been no fundamental developments in the art of reclaiming rubber since the basic conceptions of nearly thirty years ago. This is essentially true and improvements in processing have been confined mainly to the adaptation of more efficient manufacturing apparatus. But there has been progress in the raising of quality standards as a result of technical control and a better appreciation of just what characteristics constitute a valuable rubber substitute. The day has just arrived when the research chemist and the engineer have joined forces in a tardy campaign to attempt really to regenerate vulcanized rubber.

Present-day processes never reimpart the two properties of solidity and elasticity exhibited by raw rubber. Vulcanized rubber, especially after long use, has undergone such complex physico-chemical changes that we may never restore it to its original state, though it is certainly not beyond the realm of possibilities in this day of seeming miracles.

Just as vulcanizing is more than the result of the combination of rubber and sulfur, so the removal of the combined sulfur may not be expected to reimpart automatically the properties of the original rubber. When Spence[6] removed a large portion of the combined sulfur from vulcanized rubber with aniline-sodium he obtained a plastic material probably due to the softening effect of the aniline. Dubosc[7] did not obtain a plastic product when he effected the removal of over 50 per cent of the combined sulfur from vulcanized rubber by boiling it in a solution of hexamethylenetetramine. It seems that in the devulcanizing process we have to deal more with depolymerization or disaggregation; and if the removal of combined sulfur should coincidentally restore vulcanized rubber to something like its original condition, we must look farther than a method such as the alkali process or any of the proposed schemes described in the hundreds of patents on the subject.

Solvent processes cause depolymerization to a high degree, as is shown by the changes in viscosity. The solvent dis-

[6] U. S. Patent 1,235,850 (1917).
[7] *Caoutchouc & gutta-percha*, **15**, 9440 (1918).

solves the depolymerized materials and the product tends to be too soft and tacky for ordinary use. Some modification of Bary's[3] osmotic process in which he employed xylene may be the answer. Catalysis will no doubt play a principal role in true regeneration. The problem merits the attention of the research chemist in coördination with his efforts to learn the mechanism of vulcanization, if for no other reason than that the solution of either may lead to the discovery of the other.

Acknowledgment

The writer wishes to express his thanks to J. H. Coultrap, C. H. Smith, and R. W. Moorhouse, of the Goodyear organization, for assistance in preparing this paper, and to the officials of the Philadelphia Rubber Works for information which they kindly gave.

[3] Dubosc and Luttringer, "Rubber, Its Production, Chemistry, and Synthesis," p. 40.

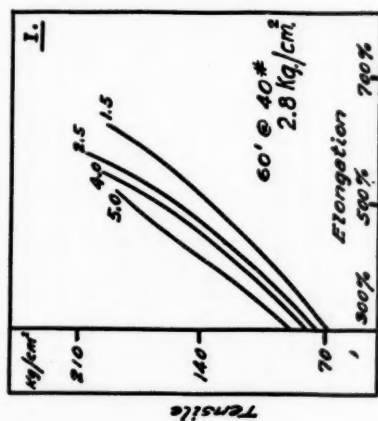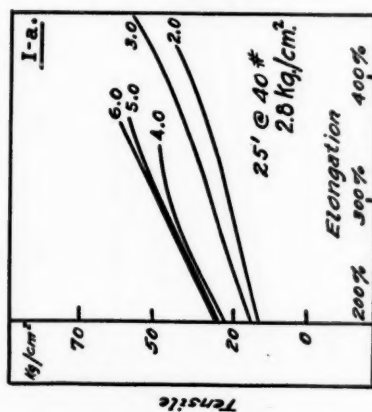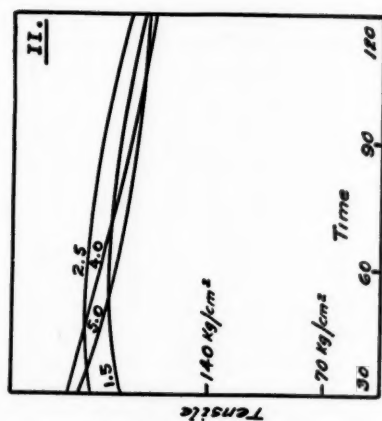# Effect of High *vs.* Low Sulfur in Vulcanizing Reclaim
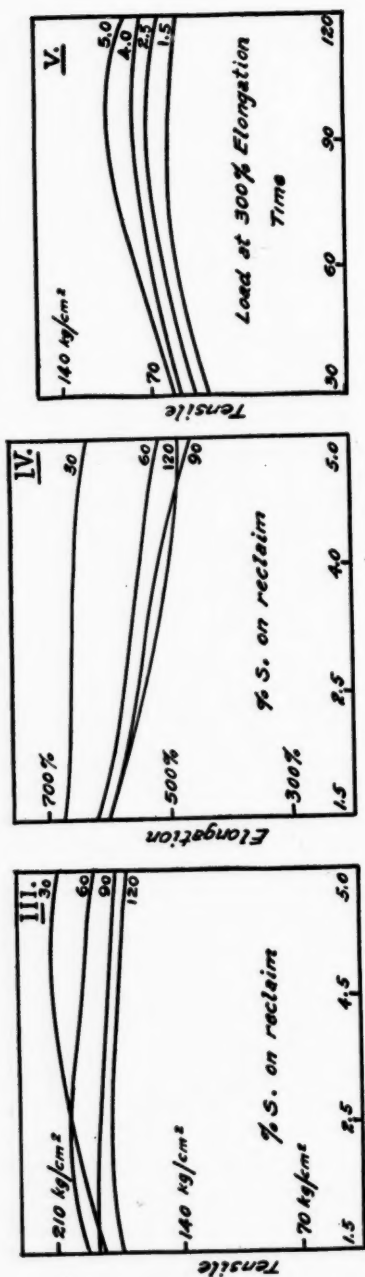
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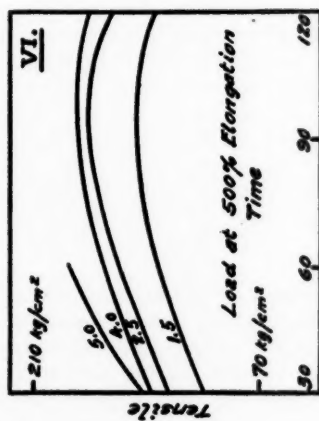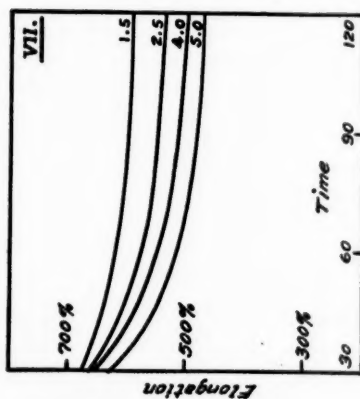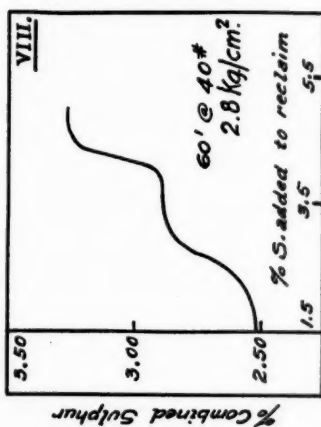
THE AKRON RUBBER RECLAIMING CO., BARBERTON, OHIO

MUCH progress has been made in determining what sulfur percentages will bring out the best quality of finished rubber, especially where organic accelerators are used, but this work has been done mostly with high-rubber stocks containing little or no reclaim. Now that reclaim has effectively entered into rubber compounding we find that there is no definite idea as to just what percentage of sulfur will give the optimum results in a compound containing a mixture of crude and reclaimed rubber. The general notion has been that approximately 4 per cent of sulfur on the total rubber content of the batch would be satisfactory in any stock with any kind of rubber-reclaim mixture, since such a value has worked well with crude-rubber compounds.   Recognizing that such a rule is obviously untrustworthy for reclaim stocks, the authors have sought a more accurate method for computing sulfur percentages. They submit this paper as merely preliminary to a subject which is vital to all compounders.   The rubber content of the reclaim is considered to be the difference between the total unit weight of the reclaim and the sum of the parts by weight of acetone extract, ash, total sulfur, and carbon black.

Experiments with Straight Reclaim Stock

A sample of 45 kg. (100 pounds) of washed alkali tire reclaim was selected, and from it all the reclaim used in the following tests was cut.   By varying the sulfur percentages from 1.5 per cent to 6.0 per cent on the reclaim in straight reclaim sulfur mixes one set of cures was obtained.   These were made at intervals of 5 minutes.   All cures were made at 142°

III. / IV. / V.

Load at 300% Elongation

Tensile — % S. on reclaim

Elongation — % S. on reclaim

Tensile — Time

C. (287° F.) in the conventional type of horizontal press. Dumbbell test strips were cut from each slab and tested on a modified Olsen tensile machine, for loads at chosen elongations as well as breaking tensiles and elongations.

The results for the 25-minute cure indicate a surprising flatness after a minimum of 3.0 per cent of sulfur is added. Percentages less than that show undercure throughout. (Plate I-a) The only noticeable change in physical properties is in the stiffening of the modulus of rigidity progressively to the maximum percentage of sulfur present. This modulus also increases as the time of cure of any one sample increases. The ultimate tensiles of the 25-minute cure pass from a minimum at 2 per cent sulfur, or below, to an approximately constant maximum from 3 per cent up to and including the maximum amount of sulfur added.

Experiments with Compounded Stock

A typical tire-tread formula was used in making up the
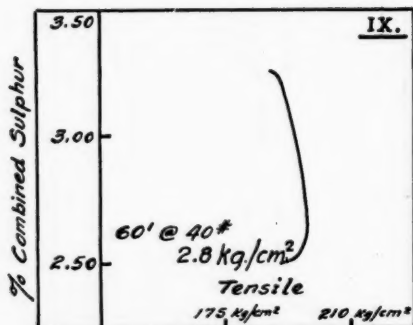
compounds for another set of cures to determine the effect of varying the sulfur in a compounded stock. Cures were made at 15-minute intervals.

FORMULA

	Parts		Parts
Rubber	35.0	Stearic acid	0.5
Reclaim	35.0	Mineral rubber	5.0
Carbon black	17.0	Sulfur	Variable
Zinc oxide	5.0	Accelerator	1.0

The sulfur percentages were varied from 1.5 per cent to 5 per cent on the reclaim. In all the compounds 4 per cent of sulfur was figured on the crude rubber present in addition to that added for vulcanizing the reclaim. Samples of the 60-minute cure for each compound were analyzed for free and combined sulfur and acetone and chloroform extracts. (Table I)

Table I—Analysis of Tread Stocks Cured 60 Minutes at 2.8 kg. per sq. cm. (40 lbs.) Pressure

(Figures in per cent)

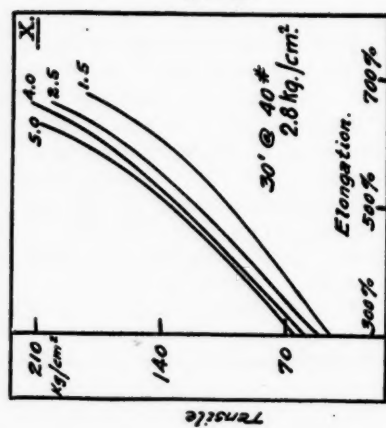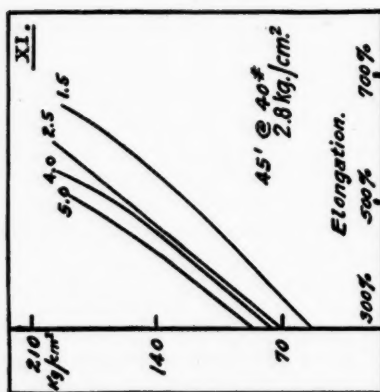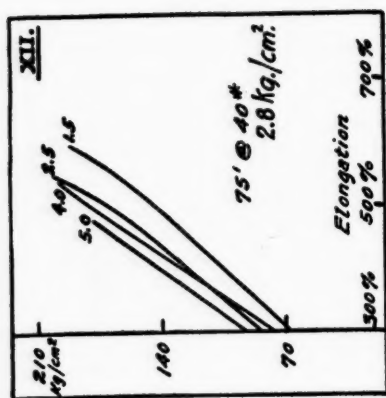| SULFUR IN RECLAIM	ACETONE EXTRACT	ACETONE EXTRACT (COR.)	TOTAL SULFUR	COMBINED SULFUR	FREE SULFUR	CHCl₃ EXTRACT
			STOCK NO. 1			
1.5	4.25	3.89	2.83	2.47	0.36	0.88
2.0	4.39	3.98	2.94	2.53	0.41	0.68
2.5	4.57	4.13	3.06	2.62	0.44	0.81
3.0	4.23	3.78	3.30	2.85	0.45	0.82
3.5	4.46	4.00	3.35	2.89	0.46	0.73
4.0	4.88	4.36	3.44	2.90	0.54	0.72
4.5	4.86	4.33	4.01	3.46	0.55	0.83
5.0	5.08	4.35	4.20	3.47	0.73	0.79
			STOCK NO. 2			
1.5	6.03	5.92	2.61	2.50	0.11	0.89
2.0	6.98	6.82	2.95	2.79	0.16	1.08
2.5	6.68	6.48	2.71	2.51	0.20	1.03
3.0	7.38	7.11	2.89	2.62	0.27	1.19
3.5	7.14	6.83	3.34	3.03	0.31	0.82
4.0	7.60	7.27	3.36	3.03	0.33	0.88
4.5	7.28	6.98	3.43	3.12	0.31	1.02
5.0	7.61	7.26	3.55	3.20	0.35	0.85

The effect of increasing curing time on the stress-strain curves is illustrated by Plates X, XI, I, XII, XIII, XIV, and XV in order mentioned.
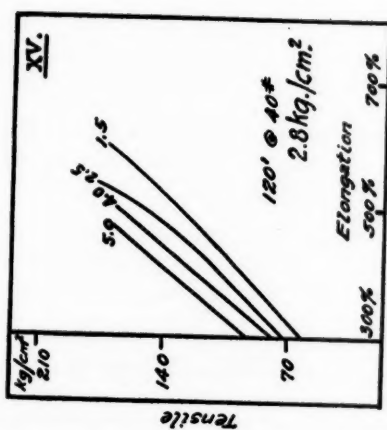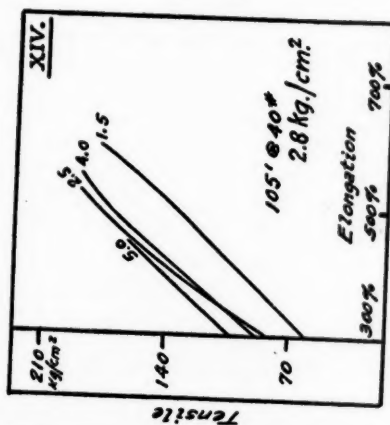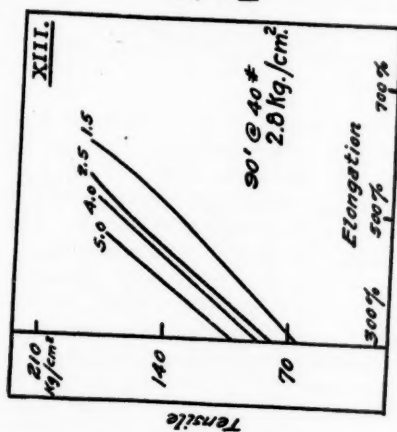
As the time of cure increases the stress-strain curves show considerable shortening and a decrease in the angle formed with the Y axis, except in case of low-sulfur compounds. Therefore, with a sulfur content of 1.5 per cent, 2.5 per cent on the reclaim, better curing conditions were obtained for a longer curing time. Larger percentages of sulfur give proportionately greater changes in the position of the stress-strain curve of the various cures.

As the percentage of sulfur is increased to a maximum of 5 per cent on the reclaim, in addition to the 4 per cent added to the crude rubber, the ultimate tensile strength increases to a maximum, then decreases for all samples of each curing period. (Plate II)

In the 30-minute cure the tensile strength increases with increase in sulfur content up to 4 per cent, but with further increase in sulfur it decreases again. In the 60-minute cure 2.5 per cent of sulfur gives the maximum tensile strength and remains in this position throughout the remainder of the cures. The tensile strength curve in this plate passes through a maximum as the percentage of sulfur increases and then decreases on further increase in sulfur. It also shows that this maximum value, 2.5 per cent, holds for a longer duration of curing time than for any other sulfur percentages used. As the percentage of sulfur increases the rate of cure increases. (Plate III)

The greatest tensile strength is given by 4.5 to 5 per cent of sulfur at 30-minute cure; 2.0 to 2.5 per cent gives the best results at 60-minute cure, and equally as good tensiles at the 90- and 120-minute cures. This indicates also, as was demonstrated before, that 2.0 to 2.5 per cent of sulfur on the reclaim content of the compound gives the best average tensiles over any chosen curing range, up to the point of

XV.

120' @ 40#
2.8 kg./cm.²

5.0
4.0
2.5
1.5

Elongation

300%   500%   700%

210 Kg/cm²
140
70

Tensile

XIV.

105' @ 40#
2.8 kg./cm.²

5.0
2.5
4.0
1.5

Elongation

300%   500%   700%

210 Kg/cm²
140
70

Tensile

XIII.

90' @ 40#
2.8 kg./cm.²

5.0
4.0
2.5
1.5

Elongation

300%   500%   700%

210 Kg/cm²
140
70

Tensile

overcure. Increasing sulfur content causes a corresponding decrease in the ultimate elongation in each cure examined. (Plate VII) Also the ultimate elongation decreases as the time of cure increases. (Plate IV) The loads at 300 and 500 per cent elongation increase as the sulfur percentage increases. (Plates V and VI)

On overcuring there is a noticeable drop, indicating reversion. There is a proportional stiffening on modulus up to a maximum at the 90-minute cure, whence there is a slight falling off in load.

In Plate VIII combined sulfur is plotted against percentage of sulfur added to reclaim, independent of that taken as necessary for vulcanizing the crude rubber present. The combined sulfur is directly proportional to the per cent of sulfur added to the reclaim. This indicates that all the above statements concerning percentage of sulfur added are proportionately true of combined sulfur percentages.

The relation of combined sulfur to ultimate tensile strength is shown by Plate IX. Here the highest tensiles come within the range of 2.5 to 3 per cent of combined sulfur, which correspond to 1.5 to 3.0 per cent of sulfur added to reclaim. (Plate VIII)

Further chemical analysis revealed that both the chloroform and acetone extracts of cured samples were constant for any given cure (Table I), and that the free-sulfur content of the cured sample increased as the percentage of sulfur in the reclaim was increased and was proportional to it.

Conclusions

To obtain the optimum results in curing compounded stocks containing whole tire reclaim, a minimum of 2.0 and a maximum of 2.5 per cent sulfur are required. This range of sulfur content, based on the total weight of reclaim in the compound besides the 4 per cent added for curing the crude rubber present, gives the flattest and longest curing range in conjunction with the highest physical qualities. Three per cent of sulfur on the straight reclaim-sulfur mix gives the maximum physical properties.

Pigment Reënforcement of Reclaimed Rubber

H. A. Winkelmann and E. G. Croakman

THE PHILADELPHIA RUBBER WORKS COMPANY, AKRON, OHIO

COMPOUNDING ingredients of many types are in use in rubber compounds and, although their effect on rubber has been extensively investigated, there has been very little work published to show their effect on reclaim alone. The behavior of reclaimed rubber in compounds which also contain crude rubber, accelerators, and pigments is well known. The presence of these variables makes it impossible to determine the effect of the pigment on the reclaim itself. In this study we propose to show (1) the effect of varying volume loadings of different pigments on a whole-tire reclaim cured with sulfur, (2) the effect of accelerators and activators, and (3) the effect of curing at lower temperatures. With crude rubber the desired physical properties may often be obtained by cure or by the combined effect of cure and the reënforcing action of compounding ingredients. Owing to the degree of disaggregation of the reclaimed rubber the effect of cure is greatly decreased and the action of reënforcing pigments is necessary to bring out the maximum physical properties of the reclaim. The soluble and insoluble phases of reclaimed rubber differ in chemical and physical properties, indicating varying degrees of disaggregation of the rubber hydrocarbon.

Reclaimed rubber affords a very good medium for the dispersion of pigments. Dispersions of pigments in a reclaim may serve a dual function in improving both the physical properties and the working conditions. A pigment, to function as a reënforcing agent, must absorb the rubber, resulting in a "drying up" effect of the more highly disaggregated portion of the reclaim. A pigment must reënforce every portion of the reclaimed rubber hydrocarbon before it can be classed as a reënforcing pigment.

The reënforcing action of pigments such as whiting, barytes, blanc fixe, clay, catalpo, zinc oxide, Kadox, thermatomic carbon, and carbon black has been studied in a whole-tire reclaim. For purposes of comparison a standard grade of mineral rubber was also used. The whole-tire reclaim used had a rubber value of 57 per cent. The same lot of reclaimed rubber was used throughout. Varying volumes of each pigment—viz., 2.5, 5, 10, 15, and 20—were added to 100 volumes of the reclaim and cured with 5 parts of sulfur. This volume-loading range insures both a minimum and a maximum loading effect. Each compound was cured for lengths of time varying from 15 to 55 minutes at 287° F. (141.7° C.). The reënforcing action of each pigment on the reclaim and the rubber hydrocarbon in the reclaim was thus observed without the presence of other factors.

Stress-strain, tensile strength, elongation, permanent set, resistance to tear, resistance to abrasion, and plasticity measurements have been made in order to correlate the effect of these pigments on each of the above factors. The abrasion tests were made on the New Jersey Zinc Company's abrasion machine.

Two methods of mixing were used to insure the best dispersion possible and to serve as a check throughout the work. In one series of experiments the pigments were added to the unfinished reclaim and then refined; the sulfur was then added. In the second series the pigments and sulfur were added to the finished reclaim on the mixing mill. Owing to the close agreement of the results obtained by the two methods only the experiments in which the pigments were refined into the reclaim will be reported. Refining versus mixing did not show marked differences in physical properties of the 5- to 10-pound batches which were used. In general, when the pigment was refined into the reclaim a higher elongation was obtained, although the tensile strength was not always increased. The refining of pigments and reclaim in factory practice gives better dispersion due to breaking up of pigment agglomerates. The results are improved physical properties and a smoother reclaim, depending upon the pigment used.

A study of the physical properties of the compounds containing various pigments shows that carbon black is the only pigment that has a marked reënforcing effect with increasing volume of pigment. Twenty volumes of carbon black still show an improvement in the physical properties. Thermatomic carbon, clays, and zinc oxides show some effect, whereas the other pigments show scarcely any. Large amounts of whiting, barytes, and blanc fixe can be compounded into a reclaim without appreciably affecting the stress-strain curve or showing a serious overloading effect.

MINERAL RUBBER—A comparison of the stress-strain curves of varying volumes of mineral rubber shows that this

material has no reënforcing value. (Figure 1) The cures become softer as the amount of mineral rubber is increased. The tensile strength decreases but slightly with increasing volumes of pigment. (Figure 2) The modulus at 200 per cent elongation, however, is almost identical with that of the reclaim alone. Mineral rubber increases the resistance both to tear and to abrasion. (Figure 3) The slight increase in the resistance to abrasion as the amount of mineral rubber is increased may be due to the fact that the true abrasion loss is not obtained because the stock becomes soft.

WHITING—The stress-strain curves of varying volumes of whiting show that it is almost inert as a reënforcing pigment. (Figure 4) There is only a slight stiffening shown in the lower part of the stress-strain curve. The tensile strength decreases with increasing volumes of whiting. (Figure 2) The elongations at break and modulus at 200 per cent elongation are identical with the blank. The resistance to tear (Figure 3) is increased slightly with 10 volumes of whiting, while the resistance to abrasion increases up to 10 volumes and then remains constant.

BARYTES—This pigment shows no reënforcing effect with increasing volumes of pigment. (Figure 5) Even with 20 volumes no stiffening is indicated and lower tensiles are obtained in each case. Barytes results in a gradual decrease in the tensile properties with increased volume loading while the modulus at 200 per cent remains almost constant. (Figure 6) A slight lowering of the elongations occurs. The resistance to tear (Figure 7) is not affected, although the resistance to abrasion is improved with each addition of pigment.

BLANC FIXE—A maximum reënforcing effect is shown with 20 volumes. (Figure 8) Its effect is very slight, however, and shows but very little improvement over the reclaim alone. Increased volume loading gives higher tensiles to 5 volumes, after which there is a decrease due to overloading. (Figure 6) A slight decrease in the elongations is also obtained. Better resistance to tear and abrasion (Figure 7) are obtained than with the reclaim alone.

CATALPO—There is a reënforcing effect without any stiffening action. (Figure 9) Higher elongations are obtained with catalpo than with the reclaim itself, showing that a further plasticizing effect may have taken place as a result of the working in of the pigment. Both the resistance to tear and to abrasion is superior to that obtained with the reclaim. A higher permanent set is observed over the full range of cures. Increased volume loading (Figure 10) gives a slight increase in tensile up to 10 volumes, after which it decreases again, while the elongation remains almost constant. Practically no effect is produced on the modulus at 200 per cent elongation. The resistance to tear (Figure 11) is only slightly increased, although the resistance to abrasion

Figure 1 — Varying Vols. Of Mineral Rubber. 35 x 287°F (141.7°C). Tensile Strength - Lbs/Sq.In. vs % Elongation.

Figure 2 — Varying Vols. Of Mineral Rubber And Whiting. Modulus At 200% Elongation. 35 x 287°F (141.7°C). Tensile Lbs/Sq.In., % Elongation vs Volumes.

Figure 3 — Varying Vols. Of Mineral Rubber And Whiting. 35 x 287°F (141.7°C). Lbs Resistance, Plasticity, Abrasion Loss vs Volumes.

Figure 4 — Varying Vols. Of Whiting. 35 x 287°F (141.7°C). Tensile Strength Lbs/Sq.In. vs % Elongation.

Figure 5 — Varying Vols. Of Barytes. 35 x 287°F (141.7°C). Tensile Strength - Lbs/Sq.In. vs % Elongation.

Figure 6 — Varying Vols. Of Barytes And Blank Fixe. 35 x 287°F (141.7°C). Tensile - Lbs/Sq.In., % Elongation vs Volumes.

Figure 7 — Varying Vols. Of Barytes And Blank Fixe. 35 x 287°F (141.7°C). Lbs Resistance, Plasticity, Abrasion Loss vs Volumes.

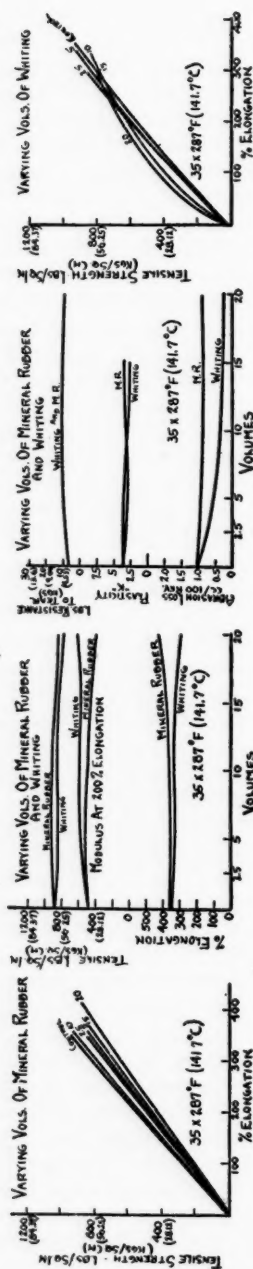Figure 8 — Varying Vols. Of Blank Fixe. 35 x 287°F (141.7°C). Tensile Strength - Lbs/Sq.In. vs % Elongation.
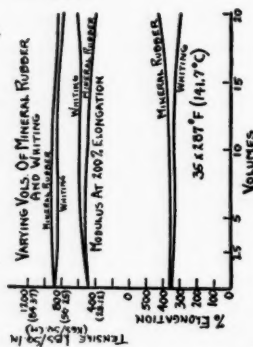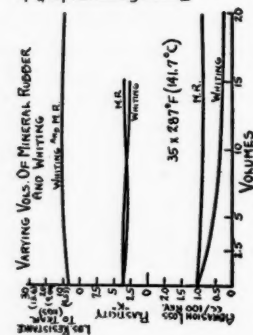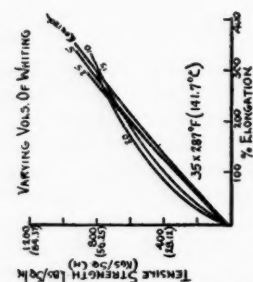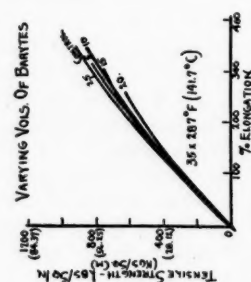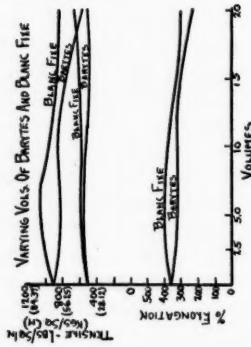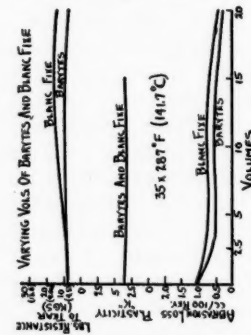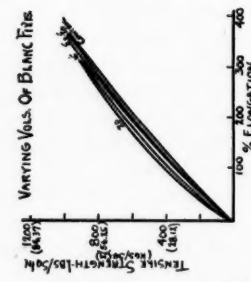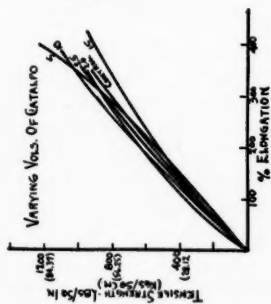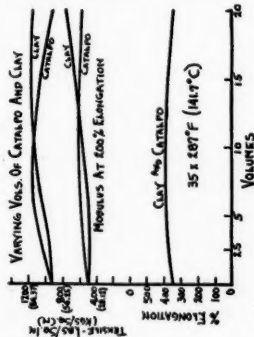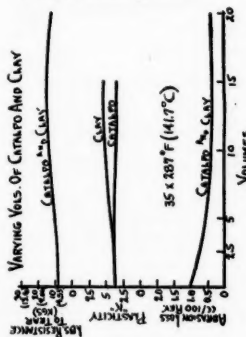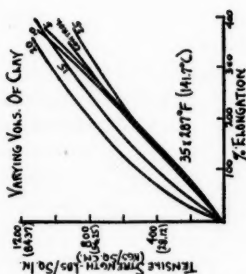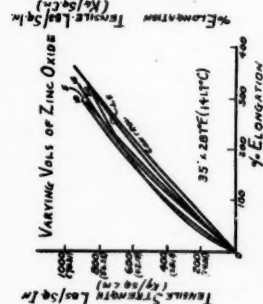
Figure 9

Figure 10
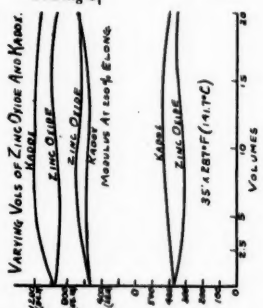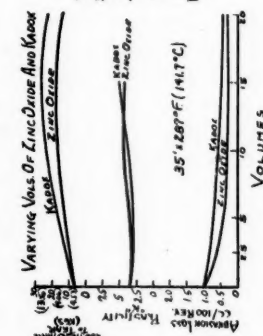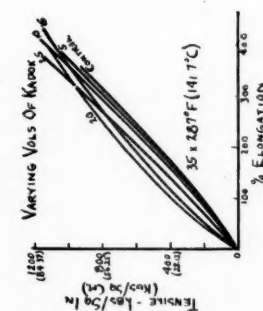
Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

is appreciably improved with each additional amount of pigment.

CLAY—A stiffening as well as a reënforcing action is shown. (Figure 12) The stress-strain curve with 2.5 volumes is lower than the reclaim alone, but as the amount of pigment is increased a decided stiffening effect is obtained, reaching a maximum of 20 volumes. The tensile strength (Figure 10) improves as the amount of pigment is increased, while the elongations remain almost constant. The modulus increases with each addition of pigment. The resistances to tear (Figure 11) and abrasion are increased slightly with increased volume loading.

ZINC OXIDE—Zinc oxide has a reënforcing effect and, although the degree of stiffening increases with each addition of pigment, this effect is not very marked. (Figure 13) The tensile strength (Figure 14) and modulus at 200 per cent increases slightly with each addition of pigment. The elongation, however, remains practically constant even up to 20 volumes. The resistances to tear and abrasion increase slightly. (Figure 15)

KADOX—There is a decided reënforcing effect and in every instance the ultimate breaks are higher than those obtained with the reclaim alone. (Figure 16) Increased volume loading has little effect on the tensile strength (Figure 14) beyond 5 volumes, although there is an appreciable increase up to this point. The modulus at 200 per cent remains almost constant up to 20 volumes. Very little effect on the elonga-tions is observed. The resistance to tear (Figure 15) and abrasion increases with each addition of Kadox and, in every case, is better than that obtained with the reclaim.

THERMATOMIC CARBON—The stress-strain curves with varying volumes of thermatomic carbon show decided reënforcing effect in reclaimed rubber. (Figure 17) The degree of stiffening is proportional to the amount of pigment added. Increased volume loading (Figure 18) gives only a slight improvement in tensile strength and the effect on the elongation is almost negligible. The modulus at 200 per cent elongation and the resistance to tear (Figure 19) and abrasion increase with each addition of pigment.

CARBON BLACK—This material gives higher physical properties in every instance than the reclaim alone or any of the other compounding ingredients. (Figure 20) The reënforcing effect increases in proportion to the amount added. The tensile strength (Figure 18) increases with each addition of carbon black. With none of the other pigments does the modulus at 200 per cent elongation show such a marked increase with each addition of pigment. The resistances to tear (Figure 19) and abrasion are very much higher than those obtained with any other pigment.

PLASTICITY—Plasticity measurements were made on the Williams plastometer on the sample of reclaimed rubber and on the reclaim containing 5 to 15 volumes of the

various pigments. (Table I) In preparing the sample
for test the reclaim is warmed by several pasess through
a cold mill with a setting of $^3/_{16}$ inch (5 mm.). The warmed
stock is calendered as thinly as possible and is plied
up to a thickness of about 14 mm. The plies are firmly
pressed together to exclude air. A pellet having a volume
of 2 cc. is used for each determination.

Table I—Plasticity Measurements

ADDED PIGMENT	5 VOLUMES		15 VOLUMES	
	N value	Plasticity K	N value	Plasticity K
Mineral rubber	0.746	2.72	0.643	3.06
Whiting	0.521	3.91	0.569	3.84
Blanc fixe	0.747	3.69	0.569	3.84
Barytes	0.711	3.32	0.637	3.66
Clay	0.581	4.18	0.863	5.63
Catalpo	0.813	4.21	0.721	4.13
Zinc oxide	0.659	3.55	0.829	4.60
Kadox	0.668	3.32	0.531	4.76
Thermatomic carbon	0.963	3.38	0.718	3.53
Carbon black	0.663	4.09	0.527	6.36

	N value	Plasticity K
Reclaim (no pigment)	0.680	3.53

The mixtures containing mineral rubber have higher plas-
ticity than the reclaim itself. Five volumes of barytes
and thermatomic carbon give higher plasticity than the
reclaim itself, but with 15 volumes the results are practically
the same as with the reclaim alone. Five volumes of whiting,
catalpo, and zinc oxide decrease the plasticity of the reclaim,
although the addition of 15 volumes causes no further de-
crease. Clay, Kadox, and carbon black show a marked
decrease in plasticity with increased volume loading.

The plastometer measures the resistance to flow at a given
temperature and load. It does not measure the nerve or
working properties of a rubber compound. It is possible
for a rubber compound to show a high plasticity and yet
have poor working properties due to nerviness.

METHODS OF MIXING—A comparison of the two methods
of mixing which were used is illustrated in Figures 21, 22,
and 23 for Kadox and carbon black. The tensile and elonga-
tion in each case check well within experimental error.

Effect of Accelerators

The effect of accelerators and an activator such as zinc
oxide on the physical properties of a whole-tire reclaim
containing varying volumes of whiting, clay, Kadox, and
carbon black was determined. Diphenylguanidine and
Safex were used as accelerators and the compounds were
cured at 287° F.(142° C.) and 267° F. (131° C.), respectively.
We therefore have the effect of reënforcing pigments with
accelerators at both a high and moderately low temperature.

The physical properties of the reclaim containing varying
volumes of Kadox with diphenylguanidine as the accelerator
are the same as those obtained when no accelerator is used,
with the exception of 20 volumes of Kadox which shows a
slightly higher stress-strain curve. (Figures 24 and 25)
Safex at 131° C. does not affect the rate of cure but increases

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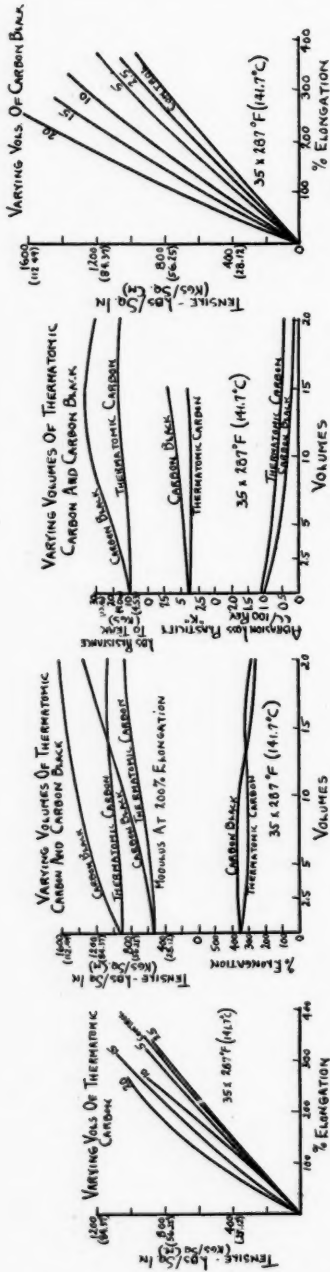
Figure 20

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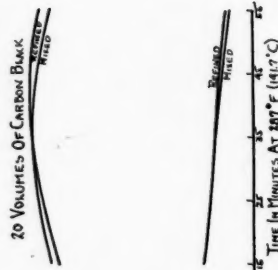
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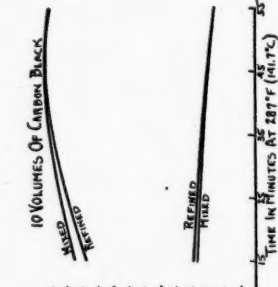
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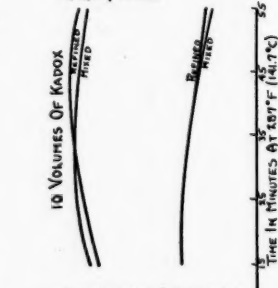
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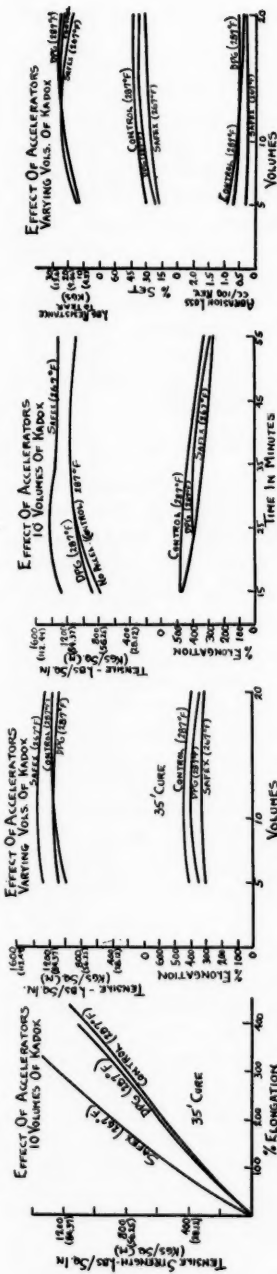
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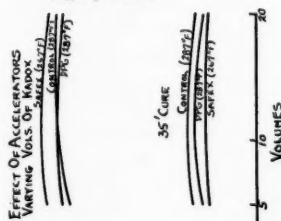
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Figure 24

Figure 25
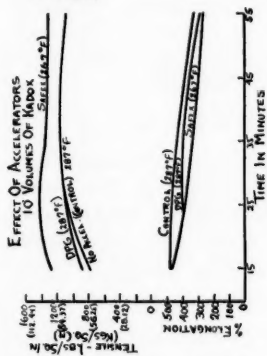
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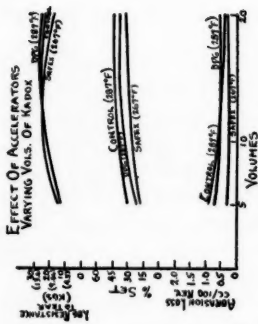
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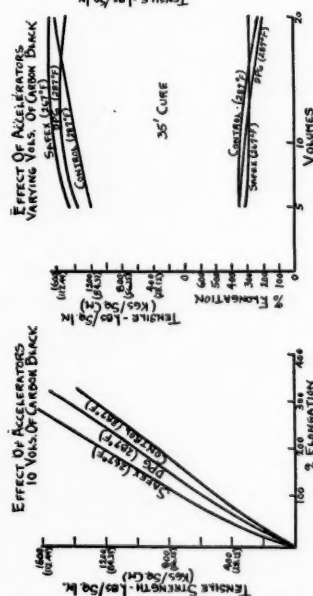
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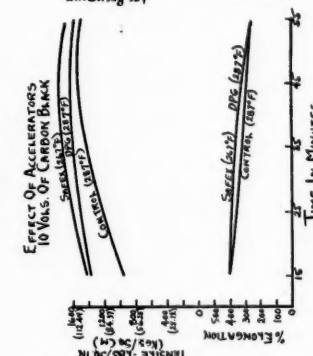
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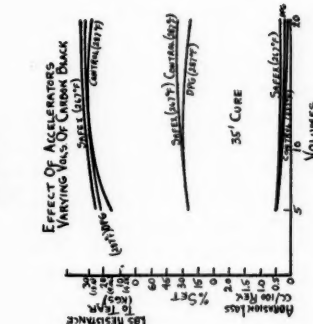
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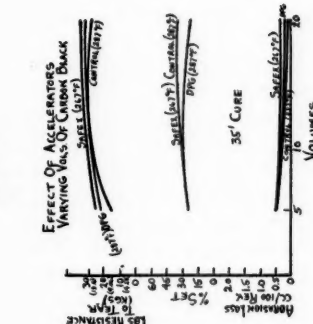
Figure 31

the tensile strength (Figure 26) and resistance to abrasion. (Figure 27) Safex gives a very much higher stress-strain curve, accompanied by a lower elongation. It has no effect on the resistance to tear.

Diphenylguanidine and Safex increase the rate of cure and improve the tensile strength of a whole-tire reclaim containing varying volumes of carbon black. (Figures 29 and 30) The resistance to tear (Figure 31) is slightly improved, whereas the accelerators give a higher stress-strain curve with 10 volumes of carbon black (Figure 28), but with 20 volumes Safex does not give any higher stress-strain curve than when no accelerator is used. This is probably due to the degree of cure obtained at the lower temperature.

Safex in a whole-tire reclaim containing varying volumes of clay or whiting gives improved tensile strength, resistance to tear and abrasion, and a higher modulus. The rate of cure is increased. Diphenylguanidine has very little effect other than increasing the rate of cure.

Effect of Low-Temperature Curing

It is logical to ask what benefits may be expected from low-temperature curing of a reclaim which in the course of its manufacture has been subjected to temperatures ranging from 350° to 385° F. (177° to 196° C.). The results of this study show that there is a distinct benefit to be derived by curing at lower temperatures.

Protective Paint from Rubber[1]

Harold Gray

The B. F. Goodrich Company, Akron, Ohio

A protective paint has been prepared from rubber
which can be used commercially.   The chief features
of the new paint are: (1) good adhesion to metals;
(2) resistance to acids, alkalies, corrosive gases, and
corrosive chemicals in general; (3) low permeability
to moisture, salt solutions, salt spray, etc.; (4) the
film is tough and can be bent without injury at sub-
zero temperatures; (5) the film does not flake when cut,
and rust spreads very slowly from an exposed area.

On account of its unusual set of properties, this paint
should have a wide range of usefulness, particularly in
chemical and other plants where metal parts are sub-
jected to excessive corrosive conditions.

RUBBER has long been considered for use in the paint
industry.   Certain of the physical properties of suita-
bly compounded rubber—such as resilience, resistance
to shock, low permeability to moisture, high resistance to abra-
sion, and its characteristic strength—make it a very promising
starting material. Several attempts have been made to
utilize its unusual properties.   For instance, a small amount
of rubber has sometimes been dissolved in the oil in regular
lead and oil paints.   No doubt in some cases this was for
advertising purposes only, but in others a determined effort
was made to utilize the physical properties of the rubber to
give an improved product.   Derivatives of rubber have also

[1] Presented as a part of the Symposium on Lacquers, Surfacers, and
Thinners before the Section of Paint and Varnish Chemistry at the 73rd
Meeting of the American Chemical Society, Richmond, Va., April 11 to 16,
1927.

been tried, but without much success. The chlorinated product is apparently the only one that has found any commercial application, and that is very limited.[2]

A number of patents have been issued dealing with paints and varnishes made from hard rubber.[3] Whether or not any of them ever reached the market, they did not achieve any considerable commercial success.

Heretofore the use of the rubber hydrocarbon as such has been impractical, for a number of reasons. Solutions of rubber in organic solvents, so-called "cements," are very viscous and it is necessary to use low concentrations. Dilute solutions—say 2 to 5 per cent—are difficult to handle as far as brushing, spraying, dipping, etc., are concerned. After a film has been deposited, it is not satisfactory, owing to its tacky nature, until it is vulcanized. This could be made an air-curing process, but at least several days would be required. Small objects could be cured in heaters, as is now done with baking paints, but such a process would limit the use of the paint too closely. Even were it possible to obtain a smooth, even coat wherever desired, there would be difficulty in obtaining a proper cure, as frequently considerable trouble is encountered in vulcanizing films deposited from a cement.

In the course of an extended series of investigations started by Fisher,[4] there has been perfected in the Goodrich laboratories a technic for modifying the properties of rubber hydrocarbon by means of a change other than vulcanization. A series of products ranging from a tough, horny, balata-like substance to a brittle, pulverizable material resembling shellac is made available by this treatment. The hydrocarbon (which throughout this paper will be designated as "thermoprene") is very pure and has many unusual properties which make it a promising starting material for paints. The outstanding point of interest to the paint chemist is that the concentration of thermoprene in the solvent can be as high as 10 to 20 per cent and still be within the range of good brushing products. The chief difference between thermoprene paint and those previously made with a raw-rubber vehicle is that the former resembles a lacquer in that it needs no vulcanizing or curing operation.

Properties of Rubber Paint

RESISTANCE TO CHEMICAL ACTION—The resistance to acids, alkalies, corrosive gases, and corrosive chemicals in general is very good. Examples are sulfuric acid, sulfur dioxide, sulfur trioxide, hydrochloric acid, hydrogen sulfide, sodium hydroxide, sodium hypochlorite, and calcium hypochlorite.

RESISTANCE TO MOISTURE PENETRATION—Low permeability to moisture, desirable in any paint, is shown to a re-

[2] Lamble, *Oil Color Trades J.*, **57**, 1250 (1920); *Kolloid-Z.*, **29**, 150 (1921); *Caoutchouc & gutta-percha*, **16**, 9811 (1919).

[3] British Patent 243,966 (1925) on India-rubber varnishes is an example.

[4] *Ind. Eng. Chem.*, **19**, 1325 (1927).

markable degree by films of thermoprene. A molded sheet (7 by 7 by $1/20$ inch or 18 by 18 by 0.13 cm.) gained 0.365 per cent in weight when immersed in water at $+1°$ to $+2°$ C. for 345 days. (Chart 1) Panels covered with the paint and immersed in water show practically none of the discoloration caused by moisture penetration. The importance of this very useful property is shown by the remarkable results obtained with the paint in salt water, salt spray, and under moist conditions in general.

ADHESION—Any paint to be of value must adhere firmly to the surface it covers. The high degree of adhesion of the new paint is one of its most important properties. It is practically impossible to separate the film from the underlying surface without actually cutting it. This property is valuable in a number of ways. For example, if a thermoprene film on iron is ruptured, the exposed surface will rust very quickly. The rust, however, will spread very slowly from the exposed area, because the film adheres so firmly to the metal that it will not strip back. When the film is cut with a knife it does not shatter or flake. The cut or scratch
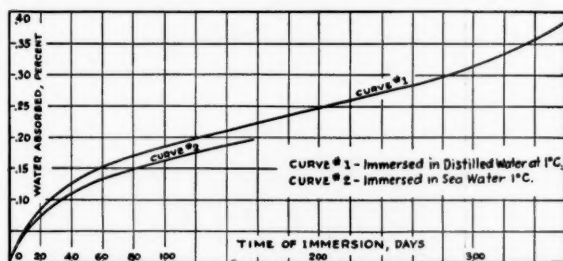
Chart 1—Resistance to Moisture Shown by Rubber Paint

is clean and only the portion actually in contact with the cutting device is affected.

ELASTICITY—The film is very elastic, as shown by the fact that a piece of steel (4 by 2 by $1/16$ inch or 10 by 5 by 0.16 cm.) covered with three coats of thermoprene and cooled to $-18°$ to $-17°$ C. can be bent double without injury to the film. A sharp blow with a hammer results in nothing more than the cutting of the film at the point of contact. Some of the films were tested at temperatures as low as $-46°$ to $-51°$ C. and showed up as well as at $0°$ C. Cutting the film when cold results in a separation only at the cut portion, with no shattering or flaking.

RESISTANCE TO TEMPERATURE CHANGES—Another rather unusual feature of the paint is its resistance to sudden temperature changes. In one series of experiments the films (on steel) were cooled in an ice-salt bath and then put on a hot plate at 115° C. After 15 minutes on the hot plate the panels were plunged into the ice water again. This cycle was repeated ten to fifteen times with no apparent effect on the films.
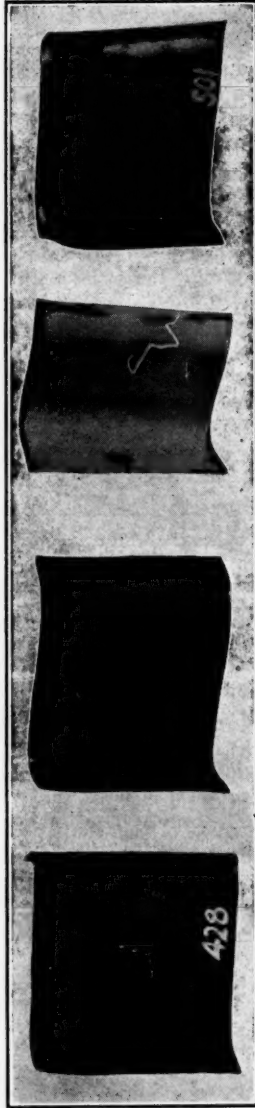
428—Thermoprene paint   458—Thermoprene paint   518—Commercial lead and oil paint   501—Commercial lacquer

Plate I—Bending Tests on 2 by 4 by 1/16-Inch (5 by 10 by 0.16-cm.) Steel Panels.   One End Bent at 0° C. and the Other at Room Temperature

PIGMENTATION PROPERTIES—Any desired pigment can be used in the paint and any color except a pure white can be obtained. The amount of pigment can be varied widely. The possible range extends from no pigment at all to as high as 250 or 300 volumes of pigment to 100 volumes of thermoprene. The practical range is yet to be determined. Good results are obtained with 70 volumes of pigment. Color may be imparted by organic dyes, using a white pigment as the filler. A very wide range of oils and softeners can be used. In some cases where a baking paint is desired, drying agents may be used. .

SOLVENT PROPERTIES—The paint should probably be classed as a lacquer, since a solvent is used which does not remain as a part of the film. In general, the ordinary rubber solvents are used—such as gasoline, toluene, benzene, carbon tetrachloride, turpentine, kerosene, etc. The solvents are varied according to the use for which the paint is intended—i. e., brushing, spraying, or dipping.

Laboratory Tests

Comprehensive tests have been conducted to determine the general characteristics of the paint. With respect to composition, the following factors were studied:

(1) Variations in physical properties of thermoprene.
(2) Effect of pigments. The more common ones were aluminum, asbestine, barytes, blanc fixe, chromic oxide, clay, gas black, graphite, iron oxide, lead chromate, lithopone, red lead, sienna, Titanox, ultramarine blue, white lead, whiting, zinc oxide, and a series of organic dyes.
(3) Variations in pigment concentration in under-coat and in top-coat.
(4) Effect of oils and softeners.
(5) Effect of driers in the drying oils.
(6) Time and temperature (compounds used for baking enamels).
(7) Surface. All the paints were tested on steel. A representative series was also tried on numerous other surfaces including aluminum, brass, and bronze (4 types), copper, Duralumin, iron (4 types), lead, nickel, tin, leaded tin, galvanized iron, zinc, magnesium, red oak, and white pine. Some tests were also made on hard and soft rubber.

Testing Program

In making those tests on composition and general properties, three panels (4 by 12 inches or 10 by 30 cm.) were made in each case, always with three coats and sometimes with four of paint. Of each set, one panel was exposed on the roof on a rack facing south at an angle of 45 degrees from the vertical, one was cut up for laboratory tests, and one was stored for reference.

General properties of films were studied in a long series of laboratory tests. These properties included:

(1) Tack, warm, and cold.

(2) Color, original, after weathering, and after treatment with various chemicals.

(3) Adhesion, at room temperature, at −18° C. and in some cases at −46° to −51° C.

(4) Bending, at the same temperatures.

(5) Cutting, at the same temperatures.

(6) Behavior toward solvents.

(7) Corrosion resistance toward various chemicals and in the salt-spray test.

(8) Weather resistance; the panels on the roof were examined from time to time to observe such effects as checking, chalking, rusting, color changes, etc.

The elaboration of this program of testing required more than two years. At one time there were over twelve hundred weather-exposure panels under observation. The con-
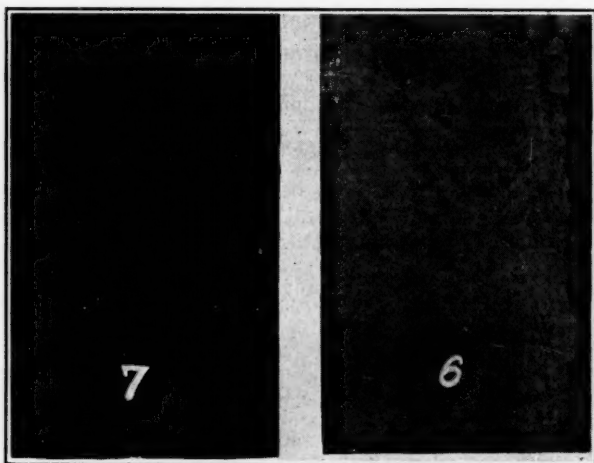
7—Lead and oil paint   6—Thermoprene paint
Plate II—Steel Panels Exposed Five Months in Salt Works

clusions drawn from this testing program are briefly summarized as follows:

(1) Physical properties of the thermoprene are uniform, subject to accurate manufacturing control.

(2) Ordinary paint pigments can be successfully incorporated into these paints over a wide volume range.

(3) Although oils and driers mix well with the paints, there is little advantage to be gained from their use.

(4) As in the case of ordinary paints, baking hardens the film.

(5) Both air-dried and baked films show good adhesion to most metallic and other surfaces. This adhesion persists at temperatures as low as −51° C.

(6) Direct exposure to weather and sunlight reveals a prevailing tendency toward chalking, occasional checking, and some rusting in spots.

(7) Exposure to acid and alkali and to salt spray indicates that thermoprene has exceptional protective properties.

Small-Scale Commercial Tests

The laboratory and roof experiments were supplemented by a series of semicommercial tests tending to show the type
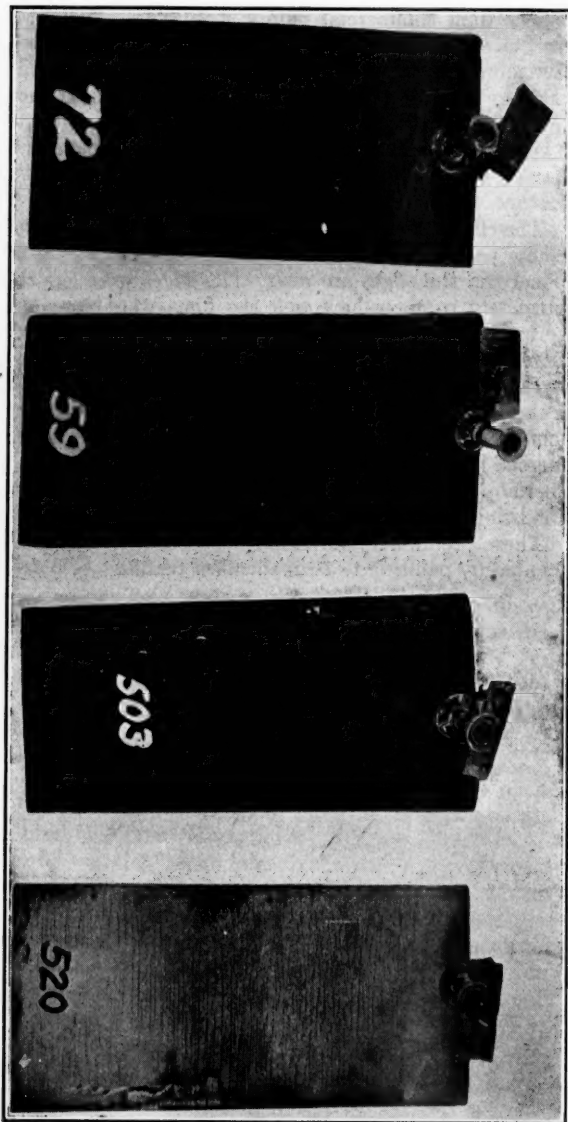
72—Thermoprene paint   59—Thermoprene paint   503—Commercial lacquer   520—Commercial lead and oil paint

Plate III—Panels in Salt Spray

of service for which the paint is best adapted. For example, there has always been a great deal of trouble in obtaining a paint which would protect the metal in a salt works. Several test panels and test sections of metal work in such a factory showed that the thermoprene paint stood up much better than commercial paints that had been used before. In Plate II two panels are shown that had been exposed for five months. Panel 7 was covered with a lead and oil paint, and is completely rusted. There are a few small rust spots on panel 6, which was protected by a thermoprene paint. These rust spots are due to pigment agglomerates, which have now been eliminated by improved methods of manufacture.

The effect of salt spray is further brought out in Plate III. These panels were cut from a 4 by 12 inch (10 by 30 cm.) panel and the edges are raw. The edges were left this way purposely to show how well the films would prevent rust-spreading. There is practically no spread of rust from the edge of the thermoprene paint panels 72 and 59.

In a cooling tower where the spray of steam and cooling water from tire vulcanizers was blown against a series of louvres in a fine spray, at the end of nine months the commercial paints were practically all destroyed, while a few thermoprene paints of a particular composition were in good condition at the end of sixteen months.

These preliminary development tests are now being augmented by painting tests in chemical plants.

Effect of Certain Metallic Salts on the Aging of a Tread Compound[1]

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AMONG rubber technologists it is generally accepted that certain metallic salts, such as those of manganese and copper, are deleterious to the aging of vulcanized rubber. A search through the literature does not disclose any quantitative test data for stocks containing salts of these metals. The higher fatty acid salts of copper, manganese, iron, and mercury were chosen for investigation, because they disperse well into rubber and because there is a possibility that these materials might accidentally be present in such softeners as palm oil, stearic acid, pine tar, and petroleum products used in rubber compounds.

Burghardt[2] was the first to refer to the poor aging of stock treated with copper oxide in the presence of olive oil. Much has been written on the cause of tackiness in crude rubber due to the presence of manganese[3] and copper salts.[4] Thomson and Lewis[5] have shown that solutions of any one of a number of metallic salts painted on the surface causes the destruction of acid-cured rubber when heated in an oven at 60° C. (140° F.). Their conclusions were drawn from appearance and from hand tests. Salts of the four metals considered—iron, copper,

[1] Presented before the Division of Rubber Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] *India Rubber J.*, **5**, 169 (1889).

[3] Bruni and Pellizola, *Giorn. chim. ind. applicata*, **3**, 451 (1921).

[4] Van Rossem and Dekker, *Ind. Eng. Chem.*, **18**, 1152 (1926).

[5] *India Rubber J.*, **7**, 328 (1891).

mercury, and manganese—have all been used as catalysts of either oxidation or reduction in various media and under various conditions. All these metals form at least two oxides. Mackey and Ingle[6] have shown that the soaps of these metals and various others serve as driers in oils. This is claimed to be due to intermediate peroxide formation. Such peroxides, if formed in rubber compounds, might have a marked influence on their aging qualities.

Procedure

In order to avoid variability in milling, portions of a 200-pound batch of the basic tread stock, mixed on a large mill, were blended on a laboratory mill with the proper amount of master batches of the various salts consisting of 90 per cent basic stock and 10 per cent of the salt in each case.

Composition of Tread Stock

	Per cent
Rubber	60.0
Sulfur	2.5
Zinc oxide	5.0
Gas black	25.0
Softeners	7.0
Accelerators	0.5
	100.0

Since this same large batch was used for both of the master batches of the metallic salts and the test stocks, there was no difference between one test recipe and another except for the amount of metallic salt added. The samples were cured in a press for 45 minutes at 149° C. (300° F.). The samples were aged in a Bierer-Davis oxygen bomb at 300 pounds (20 atmospheres) pressure and 70° C. for 48, 96, and 144 hours. They were also aged in the Geer oven at 70° C. for 5, 9, and 14 days. A badly aged piece of stock containing copper or manganese salts from the bomb was hard and stiff, while the strips from the oven were merely weakened, with relatively little change in flexibility. (See Figures 1 and 2.)

A sample of the cured basic compound corresponding to the above recipe painted with copper chloride solution also aged badly in the bomb. A coating of the catalyst does not, therefore, form a protective film of oxidized rubber which prevents further deterioration in this type of test.[7]
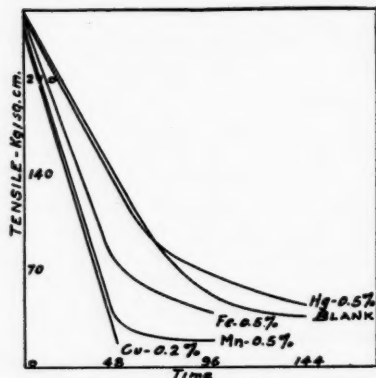
Figure 1—Change in Tensile in Aging Bomb at 70° C. Due to Presence of Metallic Salts

[6] J. Soc. Chem. Ind., **36**, 317 (1917).

[7] Williams, Ind. Eng. Chem., **18**, 369 (1926).

Data on Metallic Salts in Stock

Press cure, 45 minutes at 149° C. (300° F.). Tensile in kg. per sq. cm; elongations in per cent

Salt in Stock (*Per cent*)	Original		Bierer Bomb Test[a] — Time in Bomb						Geer Oven Test[b] — Time in Oven						Appearance and Feel after Bomb Test
			48 hours		96 hours		144 hours		5 days		9 days		14 days		
	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	
Blank	259	677	172	583	79	376	50	307	211	600	182	570	98	392	Remains soft
Cupric stearate:															
0.001	249	683	110	423	57	288	43	218	174	457	128	397	88	255	Same as blank
0.005	249	685	128	535	44	307	55	328	175	547	131	475	90	345	Same as blank
0.01	237	690	115	510	39	332	39	248	166	500	135	492	92	350	Same as blank
0.05	265	685	59	325	48	120	44	93	170	427	110	367	81	270	Same as blank
0.1	256	709	47	339	48	9	Deteriorated		177	565	91	325	91	340	Brittle
0.2	247	685	23	0	Deteriorated				179	552	87	325	84	320	Brittle
0.5	255	673	Deteriorated						174	540	86	333	84	310	Brittle
Blank painted with CuCl₂ soln.	259	677	123	505	34	230	22	185	205	580	169	528	131	435	Brittle after 144 hours
Manganic oleate:															
0.1	256	665	67	368	41	288	34	205	181	545	143	470	111	407	Brittle
0.5	251	682	32	78	20	0	Deteriorated		138	490	106	413	97	378	Brittle
1.0	236	653	13	10	Deteriorated				111	455	84	362	66	303	Brittle
Ferric stearate:															
0.1	257	709	146	555	65	385	41	224	181	583	89	388	81	357	Same as blank
0.2	252	688	137	570	58	328	41	231	165	533	79	293	75	287	Same as blank
0.5	248	665	73	413	42	264	Deteriorated		124	527	99	357	61	225	Brittle
Mercuric stearate:															
0.1	261	638	122	463	67	338	47	240	208	546	169	538	122	438	Same as blank
0.5	260	627	131	498	71	355	46	230	212	545	166	517	134	418	Same as blank
1.0	267	653	117	453	65	293	48	228	219	567	174	545	128	420	Same as blank

* At 70° C. and 20 atmospheres oxygen.   b At 70° C.

The data are given in the accompanying table.

Summary

1—The effect on aging produced by the addition of low concentrations of iron, copper, manganese, and mercury salts of higher aliphatic organic acids to a tread compound was investigated.

2—The data obtained from aging in the bomb show that the presence of copper and manganese salts of organic acids in very small concentrations is harmful to the aging of rubber. As little as 0.1 per cent of either cupric stearate or manganic oleate is detrimental. Iron stearate has a less deleterious effect, but 0.5 per cent iron stearate produced much poorer aging than the blank. The mercury salts in the concentrations used—0.1 to 1.0 per cent—did not affect the aging so noticeably as the other salts.

3—The effects of aging in the Bierer-Davis bomb and in the Geer oven are markedly different, both as to tensile strength and the hardening of the test strips. The bomb test at 70° C. was much more severe than the oven test at the same temperature. Further investigation will be made to determine which type of artificial aging test most nearly corresponds to the natural aging of these stocks.
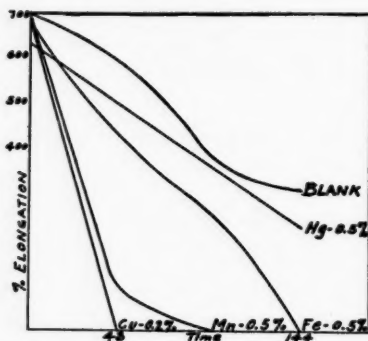
Figure 2—Change in Elongation in Aging Bomb at 70° C. Due to Presence of Metallic Salts

4—The presence of copper chloride on the surface of the test strips exerts a deteriorating influence on the stock in the aging bomb. The effect is similar to that obtained when copper stearate is compounded into the stock.

Chemical Unsaturation of Rubbers Vulcanized with Polynitro Compounds and Benzoyl Peroxide, and Its Possible Bearing on Vulcanization[1]

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STUDIES on the chemical unsaturation of ordinary vulcanized rubber show that vulcanization has caused no change in the unsaturation of the rubber hydrocarbon beyond that which can satisfactorily be accounted for by the chemical combination of sulfur on the basis of one atomic equivalent of sulfur to a C_5H_8 group.[4] If such is the case with sulfur vulcanization, it becomes very desirable to know whether there is any change in the unsaturation when rubber is vulcanized with substances other than sulfur—namely, polynitro compounds and benzoyl peroxide.[5] Do these

[1] Presented before the Rubber Division at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927. Received October 25, 1927.

[2] Present address, U. S. Rubber Co., 561 West 58th St., New York, N. Y.

[3] Present address, Lehigh University, Bethlehem, Pa.

[4] Spence and Scott, *Kolloid-Z.*, **8**, 308 (1911); also private communication from Kemp, author of the Kemp-Wijs method for the determination of the rubber hydrocarbon, *Ind. Eng. Chem.*, **19**, 531 (1927); and unpublished work of the writers.

[5] Ostromislenski, *J. Russ. Phys. Chem. Soc.*, **47**, 1462, 1885 (1915); *C. A.*, **10**, 1943, 3177 (1916).

substances or their decomposition products also add t the
olefin bonds and thus similarly reduce the unsaturation of the
rubber hydrocarbon, or do they simply act in a ca lytic
fashion and change the rubber hydrocarbon without ch nging
its unsaturation? In an effort to throw some light o this
interesting and intricate problem, samples of rubber vere
vulcanized with dinitrobenzene, trinitrotoluene, and be nzoyl
peroxide, and the unsaturation was determined by the
Kemp-Wijs method with iodine chloride.[4] These sa nples
dissolved with considerable difficulty, but a modified pro-
cedure, in which each sample cut into very thin pieces was
allowed to swell in the solvent for many hours, worked very
well. The results so far obtained are not so complete as
the writers would like to have them, because each one changed
his business connection before the full plans could be realized.
However, the results appeared so satisfactory that i' ' s
seemed worth while to publish the work as far as it has gone.

Experimental

(A) In a preliminary set of experiments with the two poly-
nitro compounds the pale crepe used was not previously
analyzed for its unsaturation. The value for the rubber
hydrocarbon (C_5H_8) used was an average value, 91.7 per cent.
The solution method was used in all these analyses, after
acetone extraction and drying *in vacuo* over concentrated
sulfuric acid.

Experiment (1)

	RATIO	BATCH
		Grams
Pale crepe	100	400
Litharge	9.5	38
Gas black	10.5	42
m-Dinitrobenzene	3.0	12
		492

Vulcanized 60 minutes at 141° C., 15 by 20 by 0.2 cm. (6 by
8 by $^3/_{32}$ inch) sheet; tensile, 200.50 kg. per sq. cm. (2852 lbs.
per sq. in.); elongation, 613 per cent.

Experiment (2)

	Grams
Pale crepe	100
Litharge	8
Trinitrotoluene	4[6]
	112

Mixed on a small laboratory mill; vulcanized as gravity disks.
20 minutes at 135° C.

Unsaturation Tests

		C_5H_8	DIFFERENCE
		Per cent	Per cent
(1)	Calculated	74.55	
	Found	75.24	+0.69
(2)	Calculated	81.86	
	Found	82.73	+0.87

[6] Stevens, *J. Soc. Chem. Ind.*, **36**, 107 (1917).

(1.) A new set of experiments was therefore run using an analyzed lot of pale crepe which, after acetone extraction, showed in two separate determinations, 91.77 and 91.79 per cent C_5H_8.

The samples were all vulcanized as 15 by 20 by 0.2 cm. (6 by 8 by $^3/_{32}$ inch) sheets between tin in a press for the times specified. The highest and best cures were then acetone-extracted for 48 hours, dried *in vacuo* over concentrated sulfuric acid for 72 hours, and analyzed by allowing very thin strips to swell in carbon bisulfide for 24 hours and then letting the reagent act upon them in this condition for 24 hours more at 0° C. in the dark. The calculated values all refer to the original weights before the acetone extraction.

Experiment (3)

Same recipe as (1).

| Cure (135° C.) | TENSILE | | ELONGATION |
Minutes	Kg./sq. cm.	Lbs./sq. in.	Per cent
45	197.40	2808	670 (sample analyzed)
60	190.37	2708	635
75	165.63	2356	610

Experiment (4)

Same recipe as (2), but using 400 grams of the pale crepe.

| Cure (135° C.) | TENSILE | | ELONGATION |
Minutes	Kg./sq. cm.	Lbs./sq. in.	Per cent
5	4.64	66	785
10	13.64	194	830
20	27.00	384	905 (sample analyzed)

Experiment (5)

	Grams
Pale crepe	400
Benzoyl peroxide[a]	27
	427

| Cure (135° C.) | TENSILE | | ELONGATION |
Minutes	Kg./sq. cm.	Lbs./sq. in.	Per cent
10	52.80	751	948
15	38.10	542	858
20	55.68	792	935 (sample analyzed)

All were clear, transparent, amber-colored sheets.

Unsaturation Analyses

| EXPERIMENT | | C_5H_8 | AVERAGE | DIFFERENCE |
		Per cent	Per cent	Per cent
(3)	Calculated	74.84		
	Found	74.56		
		74.00	74.27	−0.57
(4)	Calculated	81.92		
	Found	81.80		
		82.36	82.08	+0.16
(5)	Calculated	85.98		
	Found, 1 hour[a]	39.06		
	2 hours	52.75		
	20 hours	86.12	86.12	+0.14

[a] Refers to time the sample, after having been swelled in the solvent, was in contact with the iodine chloride reagent.

Discussion of Results

The preliminary set of experiments indicated that the change in unsaturation of the rubber hydrocarbon was not greater than 1 per cent. Since the unsaturation of different

lots of pale crepe often varies 1 per cent, it seemed as if there were really no change in the vulcanized samples.

The results of the analyzed lot of pale crepe calculated in terms of the percentage of C_5H_8 groups, varied from -0.57 to $+0.16$ per cent from the calculated amounts. Since a different reagent was used in each of the three cases—namely, dinitrobenzene, trinitrotoluene, and benzoyl peroxide—and under different degrees of compounding, it does not seem that such close agreement with the calculated value could be fortuitous. It must be concluded, therefore, that either there is no change in the unsaturation of the rubber hydrocarbon with these reagents, or, if there is, it is very small in amount.

Ostromislenski, who discovered these methods of vulcanization without sulfur, believed that the reaction was due to oxidation. Molecular oxygen, so far as is known, does not vulcanize rubber as sulfur does. The products formed when rubber is treated with oxygen or allowed to stand in air are very different physically, and probably chemically. Of course, sulfur does not vulcanize rubber at room temperatures except in the presence of a catalyst. Then, as, for example, with an ultra-accelerator, the air-cured, vulcanized rubber may contain as little as 0.5 per cent of combined sulfur.[7] With a catalyst such as platinum black, oxygen is absorbed by the purified rubber hydrocarbon in solution until finally an amount is absorbed equivalent to the formation of a completely saturated compound $(C_5H_8O)_x$, and if perbenzoic acid is used, the same or similar compound—it has the same empirical formula—is obtained.[8] These reactions correspond in a general way to those with sulfur. Now oxygen is very closely related to sulfur chemically, and by analogy it ought to vulcanize rubber if the proper conditions could be found. If it does and the amounts correspond to those with sulfur, then using the 0.5 per cent of combined sulfur mentioned above, as a possible minimum, the equivalent of oxygen would be just one-half ($^{16}/_{32}$) and the per cent of oxygen would be 0.25. Perhaps the polynitro compounds and the benzoyl peroxide do oxidize the rubber hydrocarbon and thus cause vulcanization. If they do, and oxygen thus adds chemically as the sulfur does, then from the data given above, the amount added must be very low—less than 0.14 per cent, since this would be the amount equivalent to the greatest deviation, 0.57, which is approximately the same as the recognized error with the Kemp-Wijs method, 0.5 per cent of C_5H_8. The ratio of oxygen to C_5H_8 is 16:68 or 0.24. No reliable method for directly determining such a small amount of oxygen in chemical combination is known.

The writers believe that the results herein given help

[7] Cranor, *India Rubber World*, **61**, 137 (1919); and unpublished observations of the senior writer.

[8] Pummerer and Burkard, *Ber.*, **55**, 3458 (1922).

to support the theory[9] that ordinary vulcanization is an unknown or undetermined type of change in the hydrocarbon involving no change in the unsaturation, and that the chemical union of sulfur is a secondary reaction producing a further change which no doubt gives properties that are very important in the manufacture of rubber goods, but which is a change of degree only, not of kind.

Acknowledgment

[9] Compare Harries, "Untersuchungen über die Natürlichen und Künstlichen Kautschukarten," p. 105 (1919).

Aging of Stretched Rubber[1]

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THE function of an accelerated aging test is to approximate quickly the ability of stocks to withstand deterioration during storage and service. The Geer oven and the Bierer-Davis bomb methods of accelerated aging are carried out on tensile strips which are not subjected to stresses. A large number of rubber articles are, by virtue of their use, and sometimes under conditions of storage, subjected to stress. For some time investigations have been in progress on the effect of aging of stretched rubber in order to distinguish between the relative merits of various compounds which are subjected to stress during service. Since an article is made of rubber in order that it will have flexibility and permit deformation, some measure should be made of the relative deterioration of compounds under stress. Data have been collected in an endeavor to correlate aging in sunlight with other accelerated aging tests on both unstretched and stretched samples. No direct relationship has been found between the aging in sunlight and the other methods, but a number of interesting facts have been discovered.

Sunlight Aging Tests

The first step in sunlight aging of stretched rubber was to expose for several weeks during the summer months four compounds initially stretched to different degrees, periodically measuring the tensile strength of test strips. Obviously,

[1] Presented before the Division of Rubber Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

Table I—Physical Data on Tread Stock—Sunlight Aging

INITIAL STRETCH

Time of Aging	0%		5%		10%		15%		30%		50%		100%	
Weeks	Kg./sq. cm. Tens.	Elong. %	Kg./sq. cm. Tens.	Elong. %	Kg./sq. cm. Tens.	Elong. %	Kg./sq. cm. Tens.	Elong. %	Kg./sq. cm. Tens.	Elong. %	Kg./sq. cm. Tens.	Elong. %	Kg./sq. cm. Tens.	Elong. %
0	283.71	646	241.43	580	211.47	570	189.35	510	207.76	520	209.72	487	204.54	460
2	245.07	590	221.06	540	188.58	500	146.16	460	172.41	460	176.82	440	169.54	400
4	236.67	553	203.42	525	187.67	508	125.58	500	144.97	500	136.15	442	146.65	400
6	215.60	567	210.29	540	203.91	500	111.58	420	136.01	447	145.32	377	128.31	330
8	218.05	537	191.45	500	212.94	540	95.13	440	121.94	450	122.04	400	122.08	317
10	219.80	570	181.93	470	114.66	365	98.42	403	115.99	420	121.52	403	110.67	320
12	213.71	550	164.71	500	106.89	405	81.69	400	96.67	447	93.45	397	75.39	300
14	192.71	540	176.12	477	145.04	440	76.37	400	86.52	400	98.70	407	76.86	307
16	182.42	500	177.73	507	113.05	373	85.05	410	88.20	397	91.14	393	55.58	283
18	189.42	517	179.62	520	88.41	373	80.43	393	90.86	400	90.65	387	74.90	267
20	180.18	510	174.44	490	109.76	385	72.31	380	87.92	420	90.85	367	69.37	257
22	183.75	517	182.21	483	125.58	385	84.00	365	90.72	377	85.89	377	73.78	307
24	174.72	487												

Table II—Physical Data on Shoe Upper Stock—Sunlight Aging

Time of Aging	0%		5%		10%		15% (INITIAL STRETCH)		30%		50%		100%	
Weeks	Tens. Kg./sq. cm.	Elong. %	Tens. Kg./sq. cm.	Elong. %	Tens. Kg./sq. cm.	Elong. %	Tens. Kg./sq. cm.	Elong. %	Tens. Kg./sq. cm.	Elong. %	Tens. Kg./sq. cm.	Elong. %	Tens. Kg./sq. cm.	Elong. %
0	201.81	520	125.30	420	130.62	440	104.58	413	143.99	420	151.06	440	147.00	420
2	174.44	497	111.79	400	113.68	423	117.25	420	127.19	430	131.95	427	116.41	417
4	168.07	467	90.09	425	94.22	434	98.56	442	110.32	450	117.32	450	108.71	434
6	113.05	462	86.38	370	84.35	377	88.97	370	99.68	367	99.54	370	81.83	360
8	156.59	440	83.09	407	80.64	400	83.02	400	88.83	417	95.97	417	55.23	305
10	152.88	477	66.15	315	70.21	440	70.91	357	94.64	360	74.62	357	21.28	165
12	120.19	463	65.87	370	61.60	377	60.55	340	60.62	350	51.31	327	8.61	260
14	126.07	440	48.79	297	61.32	367	58.38	345	55.58	363	48.44	240	All strips stretched 100% were broken after 14 weeks' exposure	
16	124.46	435	84.00	380	84.07	370	64.12	340	58.17	357	26.46	160		
18	113.68	420	59.29	347	63.28	363	59.57	350	59.57	345	20.51	157		
20	104.02	470	52.99	310	61.67	365	45.71	310	52.50	330	20.79	159		
22	139.86	477	59.64	360	61.88	340	54.39	300	37.38	290	21.70	140		
24	137.48	480												

the stress on the exposed samples became less as the stock took a permanent set under stretch. For this study a tread stock, a tube stock, a shoe upper, and a golf-ball thread rubber were used. The data on tread stock and shoe-upper stock are included in this report (Tables I and II, and Figures 1 and 2). In general, it was found that during the first few weeks deterioration was more rapid at low elongation than at high elongation. There was a reversal of this condition during the last weeks of the test; that is, the high elongations showed the greatest deterioration. This is probably due to the fact that when the samples under greater tension began to crack the cracks opened wide, exposing fresh surfaces to bright light, whereas the cracks in samples under weak tension were not pulled wide open and the fresh surfaces at the bottom of the cracks were shadowed from direct sunlight. The more severe cracking at low elongations during the early weeks of exposure was striking and the order of intensity as determined by visual inspection was confirmed by the tensile results. This was the principal result of the first set of experiments.

Comparison of Sunlight with Geer and Bierer Aging Tests

The next step on a larger scale was a comparison of stretched and unstretched rubber in sunlight with the same compounds aged unstretched in the Geer oven and in the Bierer bomb. Several classes of compounds were treated by these methods, special emphasis being placed on the testing of treads and tubes. Here the general facts were found to be the same as in the first series of experiments. As the cracks deepen the measured thickness of the strips is greater than the actual thickness of the uncracked rubber and the tensile strength in kilograms per square centimeter is apparently less than it is actually. The tensile results based on the over-all thickness of the test strips, however, give a fairly accurate measure of the intensity of the cracking. The results were consistent with visual comparisons in each series of tests.

Table III—Geer Oven Data

TIME OF AGING	TREAD STOCK		SHOE UPPER	
	Tensile	Elong.	Tensile	Elong.
Days	Kg./sq. cm.	%	Kg./sq. cm.	%
Original	283.71	646	183.68	550
3	243.74	558	174.86	508
5	207.76	542	137.48	467
7	156.17	492	93.59	458
10	150.57	417	82.11	425
12	123.41	397		
14	99.12	358		

The compounds included in this series were tube stock, tread stock, bath cap, and brown shoe upper. An interest-

ing comparison was brought out in this series of tests. The bath-cap stock hardened much more in sunlight and in the bomb than the other stocks. The bath cap was a fast-curing, relatively highly compounded stock, and hence should tend to harden with age. Natural aging in boxes of several caps made of the same stock produced a hardening of the surface. The Geer oven aging did not cause so great a hard-

FIG. 1

ening as the other methods. (Table III) No significant relation could be found between the results from the different types of aging tests in this series.
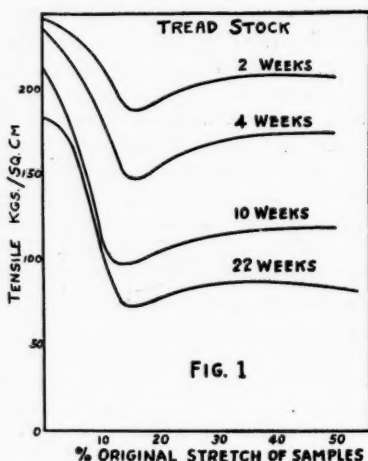
Other Types of Aging Tests

The lack of significant data from the comparison of the aging of stretched rubber in sunlight with accelerated aging of unstretched samples in the dark suggested the examination
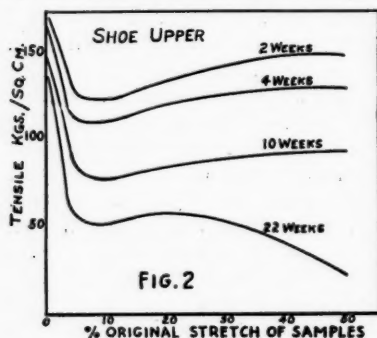
FIG. 2

of stretched rubber in other types of aging tests. One compound only was tested. This was a rubber-sulfur-accelerator mix in order to study the effect on a compound in which rubber was the principal ingredient. The strips, about $1/_{32}$ inch (0.8 mm.) thick, were stretched 0, 50, 100, 200, 300, and 400 per cent. The stretched samples were placed in sunlight, in ultra-violet light (temperature 38° to 40° C.), and in a Geer aging oven at 70° C. The source of ultra-violet light was a quartz mercury arc placed 15 inches (38 cm.) from the samples. Samples from all methods were tested after 3 and 6 days' exposure. The curves in Figure 3 show the effect of sunlight on stretched rubber is to stiffen the compound, while ultra-violet softens it. The measurement of stress-strain relations showed profound differences between the effects of these two forms of accelerated aging, although the ultimate tensiles and elongations did not make

a very clear distinction. The same series of tests shows that the oven test at 70° C. causes stiffening. Extended cracking over the surface occurred in both the sunlight and ultra-violet light tests. In the Geer oven, however, the cracks were localized along the edges of the test strips. The minimum stretch used in these tests is greater than that corresponding to maximum cracking in sunlight aging. Further work must be done, therefore, to ascertain whether deterioration takes place at a maximum rate in oven, bomb, and ultra-violet light at a definite percentage of stretch.

Sunlight aging is not satisfactory for quantitative work because the light intensity is never constant and the temperature and humidity of outside air vary. However, com-

FIG. 3

COMPARATIVE AGING
OF STRETCHED PURE GUM
STOCK
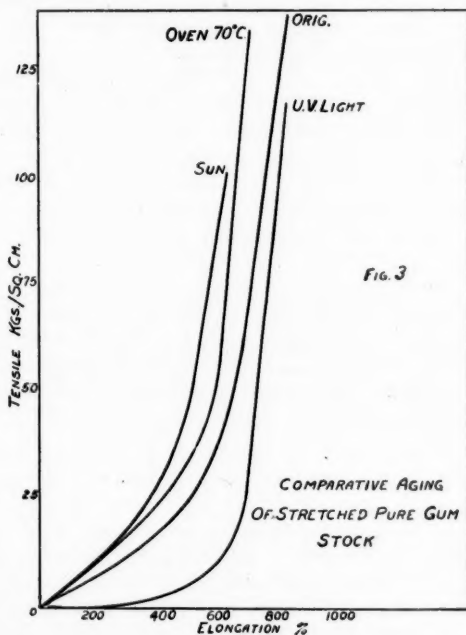
parative tests against compounds of known quality are valuable if a compound is to be used outdoors. Often a compound which ages well in the oven and bomb tests will age poorly in sunlight. For other compounds the reverse is true.

Method

Dumb-bell strips were stretched and tacked to boards at the different elongations. The stretches were measured in the narrow portion of the strip where the break would occur, so that the measured portion was stretched the amount required. The strips were removed at certain periods and the tensile and elongation determined on the basis of cross-

sectional areas, including the thickness of the cracked surface layer measured immediately prior to testing.

For sunlight aging the boards were placed on racks on the roof at an angle of 45 degrees facing southward. The Geer oven tests were run at 70° C. The Bierer bomb tests were run in pure oxygen at 70° C. under 300 pounds (20 atmospheres) pressure.

Summary

1—Sunlight aging under tension of many compounds including the following has been investigated: tire tread, shoe upper, tube stocks, golf ball thread, jar rubber, solid tire, bathing cap stock, channel rubber.

2—With some of these stocks the sunlight aging has been compared with unstretched samples by Geer oven, Bierer bomb, and ultra-violet light methods.

3—The stretching of the test strips accelerates deterioration in sunlight, ultra-violet light, and Geer oven. Stretched samples have not yet been tested in the Bierer bomb.

4—The rate of deterioration was not proportional to the degree of stretch in any of the stocks in the early stages of exposure. In sunlight there is a critical elongation for each stock at which the deterioration progresses more rapidly than at any other in the early stages of aging.

5—No direct relationship was found between the results of sunlight aging and the other methods employed.

6—Stretched strips aged in ultra-violet light were found to give softer stress-strain curves than the unaged samples, whereas sunlight aging under the same conditions stiffens the stress-strain curve.

Activity of Certain Aryl-Substituted Biguanides as Accelerators of Vulcanization[1,2]

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AS ONE chapter of a series of investigations in progress in this laboratory on the preparation and properties of aryl-substituted biguanides, their activity as accelerators of vulcanization of rubber was studied with the hope that some light might be thrown upon the relation between chemical constitution and accelerator action within this group of substances.

Substituted biguanides, α-phenylbiguanide or their carbonates or carbamates, have been patented as vulcanization accelerators.[3] Romani[4] studied the activity of α-phenylbiguanide and its salts, and concluded that, in general, the mechanism of accelerator action of these compounds was yet to be explained. Recently work has been carried out in the systematic examination of groups of pure substances as accelerators of vulcanization in order to extend the existing theories of acceleration by studying the relation between activity and the chemical constitution of the substituted radi-

[1] Received September 15, 1927.

[2] This paper is an abstract of part of the thesis submitted by Mr. Weiss in partial fulfilment of the requirements for the degree of bachelor of science in chemistry at the Polytechnic Institute of Brooklyn in June, 1927.   The vulcanization tests were carried out in the laboratory of the Metal Hose and Tubing Company of Brooklyn, and the authors take pleasure in expressing their appreciation to Robert Berkowitz, chief chemist, for his kindness in placing the facilities of this laboratory at their disposal.

[3] British Patent 201,912 (July 27, 1923).

[4] *Caoutchouc & gutta-percha*, **20**, 12005 (1923).

cals. The work on mercapto-benzothiazoles,[5] substituted guanidines,[6] and diaryl thioureas and diarylguanidines[7] are contributions to this subject. These studies have shown that activity increases, in general, with increase in molecular weight in homologous series and, among tolyl isomers, decreases from ortho to para derivatives in the case of the thioureas and from para to ortho derivatives in the case of the guanidines. Electropositive groups increase and electronegative groups decrease activity. Compounds must be basic but their activity by no means varies with basicity.

Compounds Studied

This paper presents experimental data on the activity of several aryl-substituted biguanides[8] as accelerators of vulcanization. In all cases the arylbiguanide base was used.

Biguanide is an ammono-carbonic acid and bears the same relation to guanidine that biuret does to urea—i. e., it is guanylguanidine. The aryl-substituted biguanides are ammono esters[9] and were prepared by the ammonation of dicyanodiamide (cyanoguanidine)[10] by arylamine salts. The following equation represents the reaction:

$$NH_2.C:NH.NH.C \vdots N + R\ NH_2\ HCl = NH_2.C:NH.NH.C:$$
$$NH.NH\ R\ HCl$$
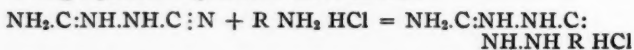
The base was obtained by treatment of the salt with an alkali, generally sodium hydroxide. Benzoxazoleguanidine was included in this study because of its close structural relationship to the biguanides and also to the benzothiazoles. The hydrochloride was prepared by the reaction between dicyanamide and o-aminophenol hydrochloride:
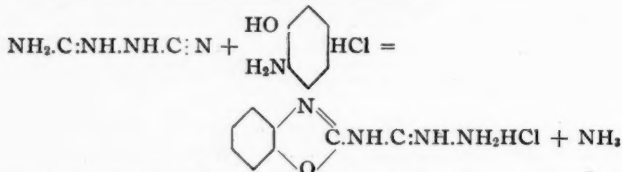
The base was obtained by treating the salt with an alkali.

Experimental

A selected batch of smoked sheet was broken down on a warm mill for 15 minutes and zinc oxide and sulfur were added to form the following mix: smoked sheet 100, zinc oxide 100, and sulfur 10 parts. One part of accelerator,

[5] Sebrell and Boord, Ind. Eng. Chem., 15, 1009 (1923).

[6] Ellery and Powers, India Rubber World, 75, 3 (1926).

[7] Naunton, J. Soc. Chem. Ind., 44, 549T (1925).

[8] The preparation and properties of these compounds and their derivatives will be described in detail in subsequent articles. See also Smolka and Friedrich, Monatsh., 9, 230 (1888); Lumiere and Perin, Bull. soc. chim., [3] 33, 205 (1905); Enrich, Monatsh., 12, 20 (1891); Cohn, J. prakt. Chem., 84, 394 (1911).

[9] Franklin, J. Am. Chem. Soc., 44, 492 (1922).

[10] Obtained from the American Cyanamid Company.

on basis of rubber content, was incorporated into this stock. After allowing to stand for 24 hours, the uncured stocks were weighed into aluminum molds and cured in slab form at 302° F. (150° C.). The cured sheets were cooled in water immediately upon removal from the press vulcanizer.
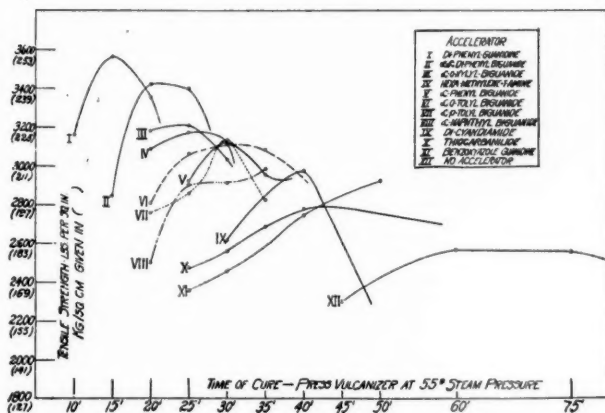
Figure 1—Effect of Various Aryl-Substituted Biguanides on Vulcanization

Table I—Cures at 55 Pounds (3.9 kg. per sq. cm.) Steam Pressure

TIME OF CURE Min.	Kg./ sq. cm.	Lbs./ sq. in.	ELONGA-TION Per cent	TIME OF CURE Min.	Kg./ sq. cm.	Lbs./ sq. in.	ELONGA-TION Per cent
	TENSILE STRENGTH				TENSILE STRENGTH		
	α-PHENYLBIGUANIDE				BENZOXAZOLEGUANIDINE		
25	205	2920	830	25	163	2323	788
30	220	3127	771	30	172	2453	813
35	207	2955	779	40	193	2743	806
40	207	2959	745	50	205	2923	800
	α-o-TOLYLBIGUANIDE				DICYANODIAMIDE		
20	197	2808	825	30	183	2613	733
25	215	3065	784	40	209	2973	725
30	218	3107	788	50	153	2185	700
35	217	3088	730	60	92	1299	500
40	206	2934	779				
	α-p-TOLYLBIGUANIDE				HEXAMETHYLENETETRAMINE		
20	194	2736	850	20	217	3084	747
25	200	2852	765	25	223	3175	706
30	218	3118	718	30	220	3134	694
35	202	2878	719	35	149	2123	613
40	177	2522	686				
	α(3,4)-XYLYLBIGUANIDE				DIPHENYLGUANIDINE		
20	223	3179	775	10	222	3161	775
25	225	3207	781	15	250	3561	756
30	213	3030	744	20	236	3355	716
35	184	2622	697	25	171	2435	607
	α-NAPHTHYLBIGUANIDE				THIOCARBANILIDE		
20	176	2500	806	25	173	2470	800
25	204	2908	800	30	179	2552	786
30	204	2910	800	35	189	2681	800
35	210	2983	756	40	196	2778	775
				50	181	2578	800
				60	197	2797	800
	α,α-DIPHENYLBIGUANIDE				NO ACCELERATOR		
15	172	2458	756	50	180	2565	780
20	241	3423	800	60	179	2559	791
25	239	3400	756	75	169	2405	750
30	184	2623	681	90	163	2320	726
				105	170	2428	738

Table II—Tread Stocks

MATERIAL	A	B	C
Smoked sheets	100	100	100
Mineral rubber	5	5	5
Zinc oxide	5	5	5
Carbon black	40	40	40
Stearic acid	1	1	1
Pine tar	1	1	1
Sulfur	3	3	3
Diphenylguanidine		1	
α-o-Tolylbiguanide			1
TOTAL	155	156	156

MIX	TIME OF CURE	TENSILE STRENGTH		ELONGATION
	Minutes	Kg./sq. cm.	Lbs./sq. in.	Per cent
CURES AT 40 LBS. (2.8 KG. PER SQ. CM.) STEAM PRESSURE				
A	60		Undercured	
	75		Undercured	
	90	113	1607	713
	120	127	1803	688
	180	120	1700	617
B	30	226	3228	722
	45	246	3500	700
	60	248	3535	669
	75	240	3420	650
	90	227	3230	642
C	30	142	2030	713
	45	199	2845	700
	60	204	2907	682
	75	209	2983	688
	90	206	2930	675
CURES AT 20 LBS. (1.4 KG. PER SQ. CM.) STEAM PRESSURE				
A		No cures made		
B	60		Undercured	
	75		Undercured	
	90	176	2502	750
	120	189	2695	719
C	60		Undercured	
	75		Undercured	
	90	124	1760	725
	120	145	2066	708

Dumb-bell test specimens were cut out and tested 24 hours after curing according to Bureau of Standards specifications.[11] Four to six specimens from each cure were tested, and in the majority of cases results were obtained from two or more individual mixes made with different preparations of the same compound.

The compounds tested were compared with stocks containing no accelerator, and with stocks containing diphenylguanidine, hexamethylenetetramine, thiocarbanilide, and dicyanodiamide. Table I records the tensile strength at break and the elongation. The results are shown graphically in Figure 1.

The activity of α-o-tolylbiguanide was further investigated in several typical commercial rubber stocks in order to obtain some data as to the effects of numerous compounding ingredients upon the activity of a typical member of this class of accelerators. The general procedure was the same as that given for the tests in the high-zinc stock, except that cures were made at 40 and 20 pounds (2.8 and 1.4 kg. per sq. cm.) steam pressure instead of the unusually high 55 pounds (3.9 kg. per sq. cm.). Comparisons of the activity of this compound were made with portions of the same stock

[11] Bur. Standards, Circ. **38**, p. 48.

containing (*a*) no accelerator, and (*b*) diphenylguanidine. The results are recorded in Tables II, III, and IV.

Discussion of Results

This work shows that aryl-substituted biguanides are accelerators of the moderate class. α-Phenyl, α-*o*-tolyl, α-*p*-tolyl, and α(3, 4)-xylylbiguanides compared favorably with hexamethylaminetetramine in the stock used for testing purposes. α,α-Diphenylbiguanide possessed somewhat greater activity than the monoaryl derivatives, but α-naphthylbiguanide, having only a slightly lower molecular weight than the diphenyl derivative, did not show such great activity as the lower homologs. This was possibly due to its unstable character, and it was, moreover, the only compound tested which imparted odor during milling and vulcanization. With the exception of α-naphthylbiguanide, the activity of these aryl-substituted biguanides varied directly with the molecular weight of the substituted radical. α-*p*-Tolylbiguanide produced more rapid overcuring than α-*o*-tolylbiguanide, thus showing a tendency of the activity to decrease from para to ortho derivatives as in the case of diarylguanidines.

Table III—Friction Stocks

MATERIAL	A	B	C
Smoked sheets	75	75	75
Whole-tire reclaim	25	25	25
Mineral rubber	5	5	5
Zinc oxide	5	5	5
Thermatomic carbon	15	15	15
Stearic acid	3	3	3
Sulfur	2.75	2.75	2.75
Diphenylguanidine		0.88	
α-*o*-Tolylbiguanide			0.88
TOTAL	130.75	131.63	131.63

MIX	TIME OF CURE Minutes	TENSILE STRENGTH Kg./sq. cm.	TENSILE STRENGTH Lbs./sq. in.	ELONGATION Per cent
	CURES AT 40 LBS. (2.8 KG.) STEAM PRESSURE			
A	75	106	1500	725
	90	135	1918	700
	105	120	1715	700
	120	120	1718	700
B	15	170	2421	763
	30	204	2910	750
	45	224	3188	719
	60	222	3167	700
	75	221	3143	650
C	15	151	2145	763
	30	209	2975	750
	45	233	3320	750
	60	234	3325	707
	75	229	3268	700
	CURES AT 20 LBS. (1.4 KG.) STEAM PRESSURE			
A	No cures made			
B	45	162	2300	775
	60	173	2460	733
	75	183	2608	757
	90	196	2790	750
C	45	117	1670	725
	60	135	1920	700
	75	165	2343	713
	90	168	2388	725

Since dicyanodiamide was the substance from which these compounds were prepared, its acceleration properties were

tested and confirmed.[12] Benzoxazoleguanidine was the least active of the compounds tested, probably owing to the presence of the electronegative oxygen in the molecule.

Table IV—Black Heel Stocks

MATERIAL	A	B	C
Smoked sheets	22	22	22
Whole-tire reclaim	40.5	40.5	40.5
Litharge	1	1	1
Clay	20	20	20
Carbon black	8	8	8
Zinc oxide	5	5	5
Sulfur	2.5	2.5	2.5
Diphenylguanidine	..	1	..
α-o-Tolylbiguanide	..	..	1
TOTAL	99.0	100	100

MIX	TIME OF CURE	TENSILE STRENGTH		ELONGATION
	Minutes	Kg./sq. cm.	Lbs./sq. in.	Per cent
	CURES AT 40 LBS. (2.8 KG.) STEAM PRESSURE			
A	15	108	1532	525
	20	108	1543	500
	30	114	1624	469
	45	104	1489	378
B	5	149	2125	507
	10	165	2343	475
	15	163	2328	400
	20	151	2045	350
	30	114	1628	238
C	5	150	2138	500
	10	166	2360	463
	15	161	2303	425
	20	151	2149	366
	30	123	1748	225
	CURES AT 20 LBS. (1.4 KG.) STEAM PRESSURE			
A	No cures made			
B	15	129	1835	525
	30	139	1975	463
	45	136	1938	416
	60	122	1740	375
C	15	140	1993	497
	30	153	2177	475
	45	150	2135	441
	60	135	1928	400

In some preliminary experiments it was found that, in the absence of zinc oxide as an activator, biguanides are very slow accelerators, as might be predicted from their close structural relation to the diarylguanidines. In the few commercial stocks tested, α-o-tolylbiguanide was found to possess the properties of a fairly good accelerator of the moderate type. It was non-toxic and milled into the batch in about the same manner as diphenylguanidine. It did not show such great activity in the tread stock as diphenylguanidine, but in the friction and black heel stocks its activity was comparable to diphenylguanidine. Possibly the use of litharge enhanced the acceleration in the black heel stock.

Extension of Work

The authors hope that further studies of the activity as accelerators of vulcanization of these and other biguanides and closely related compounds will add materially to our knowledge of the mechanism of rubber vulcanization acceleration and contemplate an extension of this work in the near future.

[12] British Patent 201,570 (July 27, 1923).

Conclusion

1—Aryl-substituted biguanides are rubber vulcanization accelerators of moderate activity.

2—The relation between the chemical constitution of the substituted radicals and the activity of the biguanides is, in general, about the same as found by other investigators for other types of accelerators.

3—α-o-Tolylbiguanide has a fairly great activity in certain commercial rubber stocks.

Effects of Ozone on Stretched Rubber[1]

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IT HAS been found that samples of vulcanized soft rubber under slight tension exposed to direct sunlight crack more severely than samples similarly exposed under somewhat greater tensions.[2] It has also been discovered that similar rubber compositions when stretched even a small amount in an atmosphere containing ozone (as low as 0.1 per cent) crack noticeably in a short time—a matter of seconds or minutes compared with a period of weeks to produce an equal degree of cracking in sunlight. As in sunlight exposure during its early stages, the degree of cracking in ozone decreases as the tension is increased beyond a definite value for each stock.

Methods of Bringing Ozone in Contact with Rubber

In the course of the experiments ozone was brought in contact with the rubber by two distinct methods.

METHOD I—By the first method 6 by 8 inch (15 by 20 cm.) sheets, $3/_{32}$ inch (2.4 mm.) thick, were held at each end by a steel clamp; one clamp was fixed to a horizontal table, while loads were applied to the other clamp. A flat metal plate was placed under the sheet of rubber and a steel rod $1/_4$ inch (6 mm.) in diameter was laid on the top side. The metal plate and rod were connected to the high-voltage terminals of a transformer. The voltage across the rubber sheet could be increased from 0 to 60,000 volts by means of

[1] Presented by F. H. Haushalter and W. N. Jones under the title "Effect of Ozonized Oxygen on Stretched Rubber" before the Division of Rubber Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] Kelly, Taylor, and Jones, *Ind. Eng. Chem.*, **20**, 296 (1928).

a rheostat in the low-voltage circuit of the transformer. At 10,000 volts the oxygen of the air in the region of the top electrode (steel rod) was broken down and ozone produced. By accurately controlling the voltage and time of exposure, by working under constant atmosphere conditions, and by guarding the apparatus from air currents, very consistent results were obtained upon repetition of the tests. Dumb-bell test sections were cut from the treated sheets so that the cracked portion was in the constricted section. The effect was then determined.

METHOD II—The second method was by the use of an ozone machine made by the United States Ozone Company. Oxygen was bubbled through sulfuric acid into the ozonizer, where it was broken down by a voltage of 10,000. The ozonized oxygen then passed into a sealed box with a glass
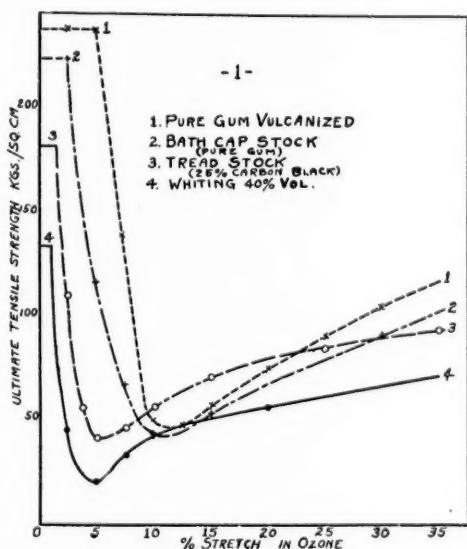

Figure 1

top. This box was 12 by 18 inches (30 by 45 cm.), and 12 inches (30 cm.) high, large enough to hold a special clamping device for stretching the samples of rubber several hundred per cent. The ozone entered one end of this box through three tubes; three small vent holes at the opposite end permitted movement of the gas through the box. Dumb-bell strips of rubber were tested at various percentages of stretch by this means under as uniform conditions of ozone concentration as could be maintained. Ozone concentrations in the box were checked at various times by potassium iodide titration. This concentration was found to be about 0.1 per cent. After considerable work by both methods the method of using high voltage in air proved preferable.

Tensile Tests

Where accurate comparisons were to be made on different stocks, two or three samples were clamped together in parallel in the clamping device, stretched a like amount, and subjected to ozone for a definite time, usually 1 minute. In determining the degree of stretch required to produce the maximum deterioration, samples were clamped together in parallel in the clamping device, one sample being stretched 2.5 per cent and the other 5 per cent. The next test would be made on one sample stretched 5 per cent and its companion 7.5 per cent; and so on. After exposure to ozone, strips were broken on the Scott rubber tester. All tensile values were calculated back to those for unstretched samples as a standard. The following machine tensiles and values calculated to the standard illustrate the method:
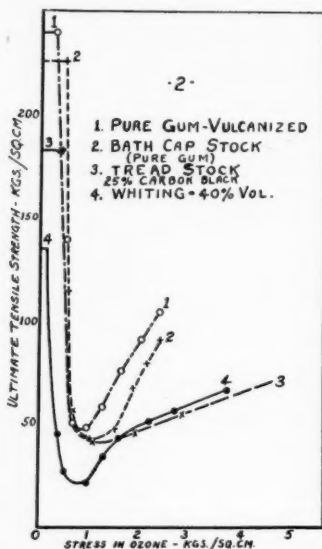

Figure 2

	MACHINE VALUES			CORRECTED VALUES		
STRETCH	Expt. 1	Expt. 2	Expt. 3	Expt. 1	Expt. 2	Expt. 3
Per cent		Kg. per sq. cm.			Kg. per sq. cm.	
0	140			140		
2.5	111.2	105.60		111.2	112.0	
5		40	42.8		42.2	42.2
7.5			47.2			46.4

That is, the corrected figure for 5 per cent is 111.2/105.6 times the machine value of 40, and the corrected figure for 7.5 per cent is 42.2/42.8 times the machine value of 47.2. This method seemed to compensate for any slight changes in ozone concentration which may have occurred. The stress-strain relations (curve sheet 5) used for translating elongation values to tension values were plotted autographically on a machine in which the load was applied by means of a long calibrated coil spring. Near the top of the spring is a clamping nut, by which its length may be changed according to the cross-sectional area of the test strip. All curves are thus drawn autographically to the same scale.

The effect of the ozone treatment is shown on curves sheets 1 and 2. Comparison of the curves for various rubber compositions indicates that the maximum cracking takes place more nearly at a definite tension than at a definite elongation. It is interesting to note, however, from comparison of the data for pure gum and tread stocks (curve sheets 1, 2, 3,

and 4) that changes in the degree of cracking and in hardness of the stretched stock seem to bear some relation to each other and to vary more nearly according to the amount of stretch than to the applied tension. The relative tension may, however, be closer in agreement with changes in hardness than the data indicate, because during the minute of exposure there is a decrease in the stresses due somewhat to the usual release in stretched rubber but more to that resulting from the cracking of the sample. In all cases the tensile figures checked the intensity of cracking as determined by visual inspection. The order in which the samples were placed on the basis of inspection was the same as that determined on the basis of tensile tests.
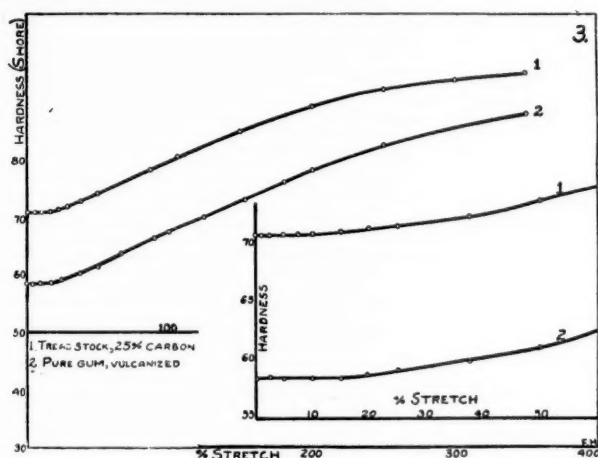

Figure 3

Hardness Tests

In measuring the hardness, a strip of rubber 1 inch wide, 5 inches long, and 0.25 inch thick (2.5 by 12.5 by 0.6 cm.) was clamped in the jaws of a tensile testing machine. The sample was stretched definite amounts—such as 2.5, 5.0, 7.5, and 10.0 per cent—the load recorded, and the hardness obtained by means of the Shore durometer. The sample was given a firm backing each time the instrument was applied. Sheets 0.6 cm. thick were used to avoid excessive thinning of the sample when stretched. The results indicate that the rubber does not at once increase in hardness as tension is applied; also, the tread stock (the stiffer of the two) begins to increase in hardness at a lower value of stretch than the pure gum stock.

The study indicates that in stretched samples there is a critical point at which the rubber is exceedingly sensitive to the oxidizing effect of ozone. As the hardness of the stock is increased by greater tension the effect of ozone is correspondingly diminished. This cracking does not occur in unstretched samples.

Effect of Ozone on Unstretched Rubber

A large number of compounds of various kinds have been subjected, unstretched, to higher concentrations of ozone,
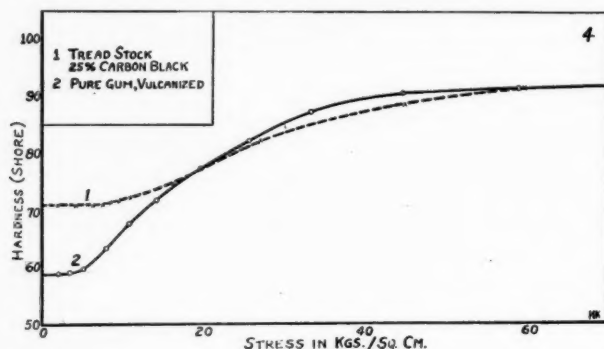

1 TREAD STOCK
25% CARBON BLACK
2 PURE GUM, VULCANIZED

HARDNESS (SHORE)

STRESS IN KGS./SQ. CM.

Figure 4

ranging from 2 to 5 per cent for 18 hours without showing any noticeable decrease in tensile strength.   For example, dumb-bell test strips of linemen's protector shield stock were exposed, unstretched, at room temperature to ozonized oxygen which contained 0.5 to 1.0 per cent ozone.   The strips were $^3/_{32}$ inch (2.4 mm.) thick and the test section 0.25 inch (0.6 cm.) wide.   The lack of change is indicated in the following table:

DURATION Hours	TENSILE STRENGTH Kg./sq. cm.	ELONGATION Per cent
0	77.4	610
0.5	73.2	570
1	75.7	607
2	73.0	560
3	73.1	567
4	74.7	600
6	76.5	617

% STRETCH

STRESS IN KGS./SQ. CM.

1 PURE GUM, VULCANIZED
2 BATH CAP STOCK, PURE GUM
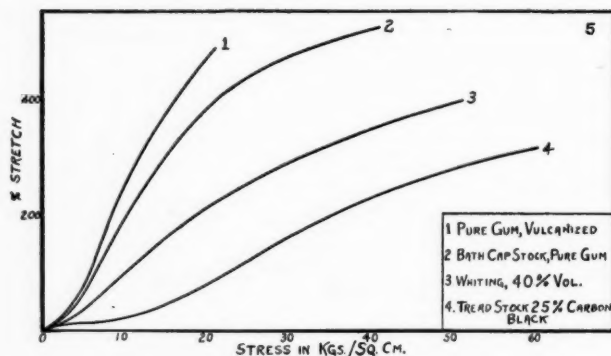3 WHITING, 40% VOL.
4. TREAD STOCK 25% CARBON BLACK

Figure 5

Strips cut from smoked sheet as received from the plantations exhibited maximum cracking at 30 per cent elongation as determined by visual inspection.

Conclusion

The similarity of the results obtained under various tensions in sunlight and in an atmosphere containing ozone is striking and may be significant of some progressive change in the structure of the rubber which renders it at a certain point unusually susceptible. The study here outlined is incomplete, but is presented in the hope that it may give other investigators an added method of studying problems connected with the structure or with the oxidation of rubber.

Analysis of a Typical Angle Abrasion Machine[1]

W. W. Vogt

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The machine employed consists of a driven abrasive wheel, the rubber test piece in ring form being pressed against the flat face of the wheel in such a manner that the plane of the ring makes an angle with the tangent of the abrasive wheel at the spot of contact. Provision is made for measuring the power consumed in abrasion by a Prony brake method.   This angle machine is essentially a constant-power machine.   The relationships between abrasion loss and time, load, speed, angle, power consumption, etc., are given.   An analysis of the forces involved is also given.

A T VARIOUS times the writer has attempted to evaluate the power consumed in causing abrasion of rubber. Two separate investigations were made; in both cases the abrasion machine used was of the angle type, wherein the periphery of a rubber ring was pressed against the flat surface of an abrasive wheel in such fashion that the plane of the ring was perpendicular to the face of the abrasive wheel and set at an angle to the tangent of the abrasive wheel at the point of contact.   The power and energy figures were obtained from readings of the current supplied to the electric motor used to drive the abrasive wheel.   On both occasions it was found that, for a wide variety of practical tread stocks, the differences in power consumption were less than the

experimental error (which was not more than 5 per cent), even though the abrasion resistance of the stocks in question varied more than twofold. It was concluded that as a practical proposition the energy concept of abrasion was of little importance in differentiating various stocks.

Recently Williams[2] showed differences between stocks of such magnitude that it was believed that had they occurred in the previous tests they would have been found. Accordingly a machine was constructed of the same type as used in the previous tests, but so arranged that the power consumption could be measured directly by the Prony brake principle used by Williams.

Description of Machine

The essential features of the machine are shown in Figure 1. The test piece, A, is mounted on the freely running bearing, B, which can be set so that the plane of the ring can make any angle (0 to 90 degrees) with the tangent of the abrasive wheel at the point of contact of the ring. The point of contact is coincident with the axis about which the holder swings. The support arms can rotate freely on ball bearings around the shaft, C, of the turn table on which the abrasive wheel, D, is mounted. This is an alundum wheel, 36 grain. A flexible strap, E, is attached to an arc of proper radius, F, and the readings of the force are obtained from the spring balance. G, reading directly to $1/4$ pound.[3] The minimum load on the test rings is, of course, the weight of the attachment (6.72 kg. or 14.8 lbs.) and this can be increased by adding auxiliary weight W. The mechanism for rotating the abrasive wheel and air jets for cleaning its surface are not shown.

The Prony brake equation applies:

$$\text{Power in kilowatts} = \frac{2\pi NFL}{4564}$$

where N = r. p. m. of abrasive wheel
 F = force = spring balance reading in kg.
 L = length of lever arm in meters = 0.21 meters

$$\text{Energy in kilowatt-hours} = \text{kw.} \times \frac{\text{time of test in minutes}}{60}$$

The abrasion values are obtained as volume loss in cubic centimeters, and from these the cubic centimeters per kilowatt-hour are obtained. These calculations are identical with those of Williams.

Description of Test Samples and Scope of Tests

Three stocks at their correct technical cure were used throughout this work; a sufficient number of rings were cured and all rings were aged at least one week before testing. Stock I is a first-grade black tread stock, stock II a second-grade tread, and stock III a third-grade stock.

[2] *Ind. Eng. Chem.*, **19**, 674 (1927).
[3] All readings of force were taken in English units, but have been converted to the metric system to conform with the publisher's policy.

The dimensions of the rubber test ring were: o. d., 8.9 cm. (3.5 inches); i. d., 5.1 cm. (2.0 inches); width, 1.8 cm. (0.7 inch).

The experimental work involves variations in angle from 5 degrees to 85 degrees, in load from 6.81 kg. to 24.5 kg. (15 to 54 pounds), and in speed from 36 to 112 r. p. m. of the abrasive wheel, corresponding to surface speeds of from 46 to 143 meters (150 to 470 feet) per minute.

Preliminary Tests

EFFECT OF TIME OF TEST—Table I shows that the rate of wear and the power consumption are independent of the duration of the test.
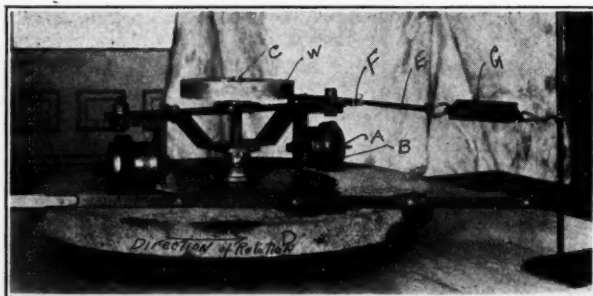

Figure 1—Angle Abrasion Machine

Table I

(Stock II; load, 16.2 kg.; angle, 20 degrees; speed, 80 r. p. m.; time, variable)

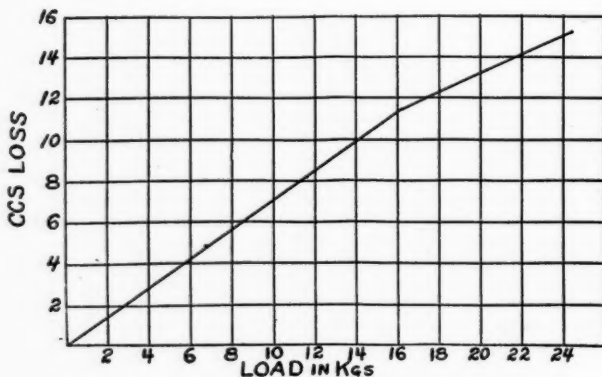| TIME	VOLUME LOSS	RATE OF WEAR	POWER
Minutes	Cc.	Cc./min.	Watts
10	11.5	1.15	95
20	22.7	1.13	95
30	34.1	1.14	95

Figure 2—Volume Loss vs. Load
(Stock II; speed, 80 r. p. m.; angle, 20 degrees)

EFFECT OF LOAD—The volume loss is practically proportional to the load, and the power consumption increases less rapidly than the load.   (Table II and Figure 2)

Table II

(Stock II; time, 10 minutes; speed, 80 r. p. m.; angle, 20 degrees; load, variable)

LOAD	VOLUME LOSS	LOSS PER KG. LOAD	FORCE	POWER	POWER PER KG. LOAD	LOSS PER UNIT ENERGY
Kg.	Cc.	Cc.	Kg.	Watts	Watts	Cc./kw-hr.
6.75	4.7	0.700	2.95	51	7.6	565
11.70	8.1	0.693	4.40	76	6.5	640
16.20	11.3	0.695	5.68	97	5.9	700
24.40	15.3	0.630	7.58	131	5.4	700

Table III

(Speed and time variable but constant (800) total revolutions)

SPEED	TIME	FORCE	VOLUME LOSS	ENERGY	LOSS PER UNIT ENERGY
R. p. m.	Minutes	Kg.	Cc.	Watt-hours	Cc./kw-hr.
STOCK II; LOAD 16.2 KG.; ANGLE, 20 DEGREES					
36	22.2	5.78	9.2	16.6	555
59	13.5	5.68	10.35	16.2	636
80	10.0	5.68	11.3	16.2	690
112	7.1	5.68	11.0	16.2	670
STOCK III; LOAD, 16.2 KG.; ANGLE, 25 DEGREES					
36	22.3	7.15	16.4	20.5	805
59	13.5	7.36	18.8	21.2	885
80	10.0	7.28	20.0	21.0	952
114	7.0	7.20	22.2	20.6	1070

EFFECT OF SPEED—Table III shows that the force is independent of the speed, and since the total number of revolutions is constant the energy (kilowatt-hours) is also constant. There is a slight increase in volume loss with increase of speed and therefore the loss per unit energy also increases.

As a result of these preliminary tests the conditions adopted for further work on the effect of angle were as follows:

Load, 16.2 kg.; speed, 80 r. p. m.; time, 10 to 30 minutes
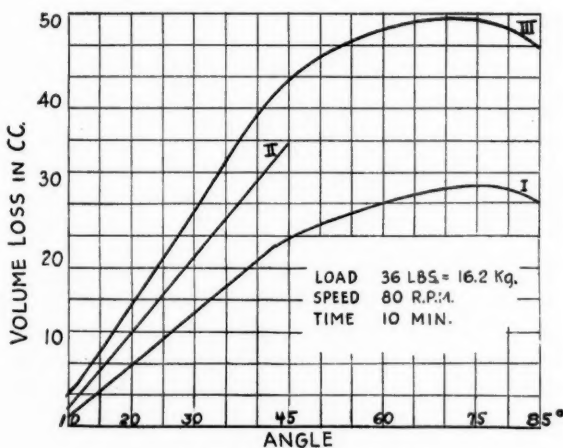
Figure 3—Volume Loss vs. Angle

Relation between Abrasion Loss and Angle

The data for the three stocks at various angles are given in Table IV. The longer time of run was used at the smaller angles, but all results are figured to a standard time (10 minutes).

These results are shown graphically. Figure 3 shows the relation of volume loss to the angle. The curves were extended to include some determinations made at very high angles. Between 10 and 45 degrees the volume loss is practically linear with respect to the angle. A few determinations indicate that at the 5-degree angle there is still a very slight but measurable abrasion taking place, but that at lesser angles the abrasion is negligible, leading to the conclusions that a certain slippage may take place without causing abrasion.

Figure 4 shows the force in relation to the angle. The points through which the curve is drawn indicate the maximum and minimum values for all three stocks. It can reasonably be said that the force, and therefore the power consumption, is identical for the three stocks.

Although volume loss was for the most part determined at one load only, the readings of force were obtained for a large number of different loads at all angles. (Figure 5)

Figure 6 shows clearly that the unit of abrasion resistance proposed by Williams— i. e. cc./kw-hr.—is not a constant of the stock, but changes tremendously depending upon the mechanical conditions other than load and kind of abrasive surface. As the angle is increased the machine accomplishes a greater amount of abrasive action on the rubber per unit of energy expended.

Figure 4—Force vs. Angle
(Load, 16.2 kg.; speed, 80 r. p. m.; stocks I, II, and III)

Figure 7 shows that there is a tendency for the relative volume losses to decrease somewhat as the angle is increased. Since the power consumed by all the stocks is a constant, this chart also expresses the relationship between the three stocks based upon the values of cubic centimeters per kilowatt-hour.

Table IV

Angle Degrees	Force Kg.	Power Watts	Energy Watt-hours	Volume Loss Cc.	Per cent	Loss per Unit Energy Cc./kw-hr.
			STOCK I			
10	2.36	41	6.8	1.45	100	214
15	4.00	69	11.6	3.65	100	317
20	5.78	100	16.6	7.20	100	434
25	7.50	130	21.7	10.80	100	500
30	8.65	149	24.9	14.10	100	562
45	11.60	200	33.3	24.50	100	736
			STOCK II			
10	Same as stock I			2.35	162	348
15				6.35	174	555
20				11.2	155	670
25				16.6	154	765
30				21.2	150	850
45				35.7	146	1070
			STOCK III			
5	Same as stocks I and II			0.35		
10				3.20	220	469
15				7.65	210	662
20				14.7	204	885
25				19.8 (?)	183 (?)	918
30				27.1	192	1090
45				45.0	184	1350

Summary of Mechanical Behavior of Angle Machine

As a mechanical device for abrading rubber this particular form of angle machine is consistent in its behavior. The following points are noted:

(1) The volume loss is practically proportional to the load.
(2) The rate of wear is constant during the test.
(3) The loss is practically independent of the speed, an increase in speed of 300 per cent causing an increase in volume loss of about 20 per cent.
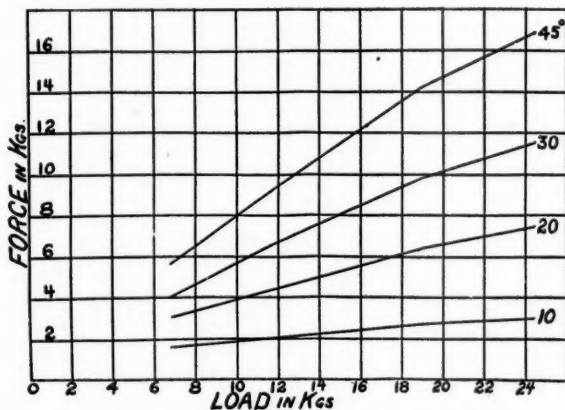

Figure 5—Force *vs.* Load for Various Angles
(Stocks I, II, and III; speed, 80 r. p. m.)

(4) The relationships between the three stocks are practically constant and independent of the load, the speed, the duration of the test, and depend only to a relatively slight extent on the angle.
(5) The over-all power is virtually a constant for a wide range

of stocks, so the test is carried out under constant power conditions.

Mechanical Forces Involved

The mechanical forces involved in this type of machine have been analyzed. (Figure 8)

F = the total force as read on the spring balance (1)
L = length of the lever arm from the center of the abrasive wheel to the center of the spot of contact of the rubber ring (2)

F can then be resolved into

C = tangential component of abrading force (3)
D = axial component of abrading force (4)
Θ = angle between plane of ring and normal to L at point of contact (5)
A = component of bearing reaction normal to L (6)
X = component of bearing reaction parallel to L (7)
N = r. p. m. of abrasive wheel (8)
W = load on test piece (9)

By taking moments about the middle support,

$$FL = C \cos \Theta L + D \sin \Theta L \qquad (10)$$
C can be evaluated by direct measurement when $\Theta = 0$
When $\Theta = 0$, $\cos \Theta = 1$, $\sin \Theta = 0$, $F = F_0$ (11)

Figure 6—Loss per Unit of Energy vs. Angle
(Load, 16.2 kg.; speed, 80 r. p. m.)

Therefore, $C = F_0$.

Rewriting (10) $F = F_0 \cos \Theta + D \sin \Theta$ (12)

Experimentally, the value of C can be neglected for all but the very low values of Θ and

$$D = \frac{F}{\sin \Theta} \qquad (13)$$

By multiplying (10) by the angular velocity $2 \pi N$ the equation then represents power instead of force.

If the coefficient of friction (cf) is defined as that which exists under abrasion conditions between the rubber and the particular abrasive surface used,
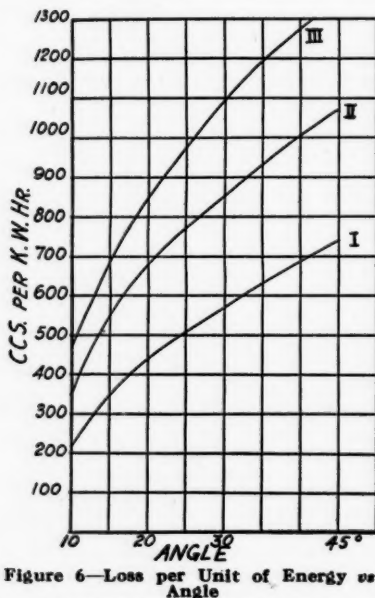
Then $cf W = D$ (14)
Since $D = 0$ when W or $cf = 0$
and $cf = D/W$ (15)

Hence the measurement of F leads to values for the power consumption during abrasion, or to values of the apparent coefficient of friction under the abrading conditions which obtain. The same analysis can be applied to Williams' machine and in this case by taking moments $D = F$.
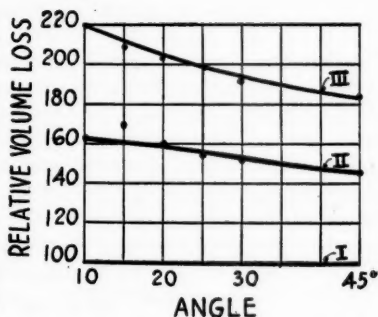

Figure 7—Relative Loss *vs.* Angle

Table V

(Stocks I and III; angle $\Theta = 0$; speed, 80 r. p. m.)

LOAD (W)	FORCE (F)	F/W
Kg.	*Kg.*	
6.75	0.14	0.0210
11.70	0.24	0.0206
16.20	0.34	0.0210
18.90	0.43	0.0220

Table V shows that F/W is analogous to the coefficient of rolling friction and is independent of the load within the limits studied.

Table VI

W	F	C	$C \cos \Theta^a$	$F_s = F - C \cos \Theta^a$	$F_s/\sin \Theta = D^a$	$D/W = cf$
Kg.	*Kg.*	*Kg.*				
6.75	3.95	0.14	0.12	3.84	7.70	1.14
11.70	6.60	0.24	0.20	6.38	12.70	1.09
16.20	8.65	0.34	0.29	8.35	16.60	1.03
18.90	9.65	0.43	0.36	9.25	18.50	0.98

^{a} Based on values of W, F, and C in kg.

Table VI shows that cf is constant within 15 per cent over a variation of load of 300 per cent; it is also the same for the three stocks. The data are taken from Figure 4 for the 30-degree curve.

Table VII gives further data with respect to widely varying angles. Abrasion losses are figured as for 800 revolutions.

Table VII

(Stock III; load (W) = 16.2 kg.; speed, 36 r. p. m. for angles above 45 degrees, 80 r. p. m. for angles below 45 degrees)

ANGLE *Degrees*	F^a	$C \cos \Theta^a$	$F - C \cos \Theta^a$	$\dfrac{F - C \cos \Theta}{\sin \Theta} = D^a$	$D/W = cf$	LOSS *Cc.*	POWER *Watts*	LOSS PER UNIT ENERGY *Cc./kw.-hr.*
10	2.46	0.34	2.14	11.60	0.70	3.2	41	765
20	5.75	0.32	5.43	15.90	0.98	14.7	114	885
30	8.60	0.29	8.41	16.65	1.30	27.0	149	1080
45	11.80	0.24	11.56	16.40	1.01	45.0	204	1330
60	14.60	0.17	14.33	16.65	1.03	48.0	251	1150
75	15.40	0.10	15.40	15.90	0.98	51.0	267	1150
85	15.85	0.03	15.82	15.90	0.98	47.0	275	1020

^{a} Based on values of W, F, and C in kg.

The values for F, and consequently for cf and power, are the same for all three stocks. The value for cf is about 1.00 over a wide range of angle.

Comparison with Williams' Machine

Some comparative tests on the three stocks were run on Williams' machine with the results shown in Table VIII.

Williams' machine does give differences in power consumption and in *cf* between the three stocks, whereas the angle machine does not. However, when the per cent of energy loss is compared with the results of the angle machine (Figure 7) the agreement is good. It is also noted that the absolute value of *cf* is greater and that the loss per unit energy is lower for Williams' machine.

Table VIII

(Load (W) = 3.74 kg.; time, 20 minutes; r. p. m., 37)

Stock	Volume Loss		Power	D	$D/W = cf$	Loss per Unit Energy	
	Cc.	Per cent	Watts	Kg.		Cc./kw-hr.	Per cent
I	1.37	100	15.4	6.36	1.70	268	100
II	1.86	136	14.0	5.75	1.54	402	150
III	2.14	156	12.9	5.35	1.43	495	185

There is no clear outstanding explanation of the differences in behavior between the two types of machine, particularly with reference to power consumption. The angle machine does not show differences in power consumption, but the relationships of volume loss of the three stocks are about the same as is obtained in the Williams machine by calculation of the cubic centimeters per kilowatt-hour.

A tentative explanation only can be attempted at the present time. It must be recognized that for both machines the measurement of power is an over-all measurement. In Williams' machine the abrasive action is a straight scrubbing action and the energy consumed is split as follows:

(1) That which appears as heat due to surface friction without causing abrasion.

(2) That which appears as heat due to hysteresis losses in the rubber.

(3) That which is actually consumed in dislodging particles of rubber.
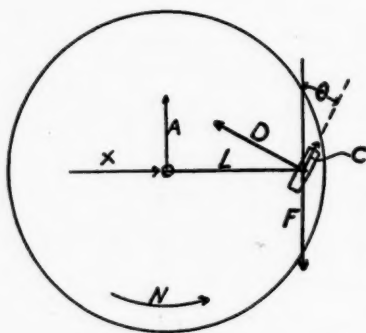

Figure 8—Plan View of Angle Machine

In the angle machine the same three factors appear together with the additional one of rotational energy, the so-called C component which can be deducted leaving the D component (power consumed in axial scrubbing), which then must be apportioned as in the Williams' machine. Factor (3) is the one in which we are vitally in-

terested, and the success which can be attained in evaluating the energy consumed in causing abrasion depends entirely on the extent to which we can make this factor approach 100 per cent of the total energy as measured. At present it seems very difficult, if not impossible, to evaluate the percentage of total energy expended in each of the three factors. However, some light may be thrown on the subject by the following experiment.

If the surface of the abrasive wheel is kept lightly covered with fine sand the energy consumption is decreased and the abrasion loss is decreased even more. By carefully controlling the amount of sand used, it is possible to maintain the energy consumption at any reasonably constant value and the abrasion loss can then be determined. Table IX gives some results on stock III.

Table IX

	Force	Power	Loss	Loss per Unit Energy
	Kg.	Watt-hours	Cc.	Cc./kw-hr.
Without sand	6.37	54.5	14.8	270
With sand	5.55	46.0	11.4	246
With sand	4.10	35.0	2.5	71
With sand	3.18	28.0	0.0	0

About 50 per cent of the energy is consumed in doing other things than causing abrasion.

Of course, it is obvious that the sand acts as a lubricant and cuts down the coefficient of friction between the rubber and the abrasive wheel. This also takes place on the road. Furthermore, it may be argued that the loose sand, instead of abrading the rubber ring, abrades the abrasive wheel, and that the work expended is used up in that sort of abrasion. This cannot be denied, but in all probability part of the energy loss in an auto tire goes towards destroying the road material.

Still another line of reasoning leads to even more striking conclusions. The energy of resilience has been taken by Wiegand as an index of the abrasion resistance of a stock. The best possible tread stock has a value for energy of resilience of about 1200 foot-pounds per cubic inch or 1000 kg-cm. per cc. In stretching a piece of rubber to the break the test strip generally fails at one place. Little imagination is required to visualize a piece of rubber which when stretched would pull to a slightly higher value and then disintegrate into a fine powder, similar to that formed during abrasion. Let us assume a value of energy of resilience of 1500 kg-cm. per cc. for such a stock.

Now we can use the index of abrasion resistance as cubic centimeters per kilowatt-hour or kilowatt-hours per cubic centimeter. A good grade of tread stock on Williams' machine gives values of 270 to 400 cc. per kilowatt-hour and on the angle type from 200 to 670, depending on conditions.

From energy of resilience figures,

1500 kg-cm. per cc. = 0.035 kg-calories per cc.

From abrasion figures,

200 cc. per kw-hr. = 4.2 kg-calories per cc.
670 cc. per kw-hr. = 1.3 kg-calories per cc.

According to these calculations it takes from 35 to 120 times as much energy to wear away rubber by abrasion as it does to break it by stretching. This means either that our measurement of over-all power of abrasion is grossly misleading as to the energy actually expended in causing abrasion, this factor being from 1 to 3 per cent of the total energy as measured, or that the mechanical principle involved in the removal of rubber elements by abrasion is widely different from that causing rupture under stress.

Conclusion

The particular modification of the angle type rotating ring abrasion machine as described in this paper can be used to obtain a figure for the over-all energy consumed in causing abrasion of rubber. The writer is undecided as to whether or not the energy which actually goes towards causing abrasion is a large enough percentage of the total over-all energy consumption to warrant any belief that the energy of abrasion has yet been measured.

Acknowledgment

Influence of the Sulfur-Rubber Ratio on the Physical Properties of Hard Rubber

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WESTERN ELECTRIC CO., INC.

Sulfur-rubber ratios from 30 to 45 appear to cover the entire range necessary for hard rubber compounds. Below a value of 30 the rubber has little strength and undergoes great deflection; above 45 the gain in strength is doubtful. Physical strength tests (tensile, transverse, and impact strengths) and deformation under heat tests are used as a basis of comparison. The tensile and deformation under heat tests are believed to be of the most value. It is hoped that these tests may be suitable for selecting rubber for various applications and for use in specifications for hard rubber.

The physical strength and deformation of hard rubber, both at room and elevated temperatures, are important in apparatus where great mechanical strength and low flow under heat and pressure are necessary.

This study was undertaken for two purposes: (1) to find the kind of rubber best suited to various types of apparatus, and (2) to introduce tests suitable for use in specifications for hard rubber. The sulfur-rubber ratios of the compounds have been varied, while all other factors have been held as constant as possible.

The sulfur-rubber ratio, which is the ratio of the sulfur to the quantity of rubber hydrocarbon contained in the crude and reclaimed rubbers in the compound and which is expressed in per cent, is perhaps the most important of the many factors involved in the production of vulcanized rubber. It is known that below a certain sulfur-rubber ratio (placed by some at 23.5)[1] vulcanized rubber assumes the characteristics which are attributed to soft rubber; above this value we have what is commonly termed hard rubber. In present-day methods, the sulfur-rubber ratio of soft rubber is seldom higher than 5. The interval between 5 and 30, we believe, is rarely used, and such compounds constitute a class of rubber frequently termed semi-hard or flexible hard rubber. While the properties of this class have not been thoroughly investigated, the compounds are known to be unstable and are of little value for commercial use at the present time. On this account, it is preferable to consider rubber as divided into the two classes, soft rubber and hard rubber. The view that the rubber molecule is apparently saturated with two sulfur atoms has been held by many investigators, chief among them C. O. Weber.[2] In this compound, having the formula $C_{10}H_{16}S_2$, the sulfur-rubber ratio is 47. Although numerous other theories have been advanced, the work with which the writer has been associated tends to substantiate the above opinion and is sufficient evidence for the purpose of this paper. It has been common practice to use sulfur-rubber ratios of greater values than 47 in the manufacture of hard rubber. As a result of the work which is presented in this paper, and similar work on compounds having higher sulfur-rubber ratios, the writer is of the opinion that this is unnecessary and that a closer control of the physical properties of the rubber can be maintained by using the lower values. The limiting sulfur-rubber ratios necessary for hard rubber

[1] *Ind. Eng. Chem.*, **18**, 73 (1926).

[2] C. O. Weber, "The Chemistry of India Rubber," p. 91.

compounds thus appear to be from 23.5 to 47. Accordingly, the physical properties of the hard rubber compounds chosen were studied, varying the sulfur-rubber ratio from 25 to 45 by intervals of approximately 5.

Consideration of Tests

In an article published last year, Dieterich and Gray[3] regarded the impact strength test as the one test which gives results most indicative of the character of the material; in this work the impact strength, transverse strength, tensile strength, deformation under heat, and softening point of the rubber were studied. The tensile, transverse, and impact tests are all measures of physical strengths of the rubber at room temperature. The softening point and deformation tests measure the deformation of the sample under heat. Thus the behavior of the material both at room and elevated temperatures was studied.

FIG. 1

APPARATUS HEAT TEST

The results given in this report were obtained at two different times, a period of approximately one year intervening. Unfortunately, there was an insufficient quantity of material remaining from the first series of tests for a second series, so that the aging properties of the rubber could not be studied. In the first series of tests the tensile data were obtained with a horizontal tensile testing machine of the pendulum type, equipped with an attachment for plotting the stress-strain diagram. In the second series the tensile data were obtained by means of a vertical floating-beam type machine. Similarly, the transverse data were secured by means of the two machines. The horizontal type of machine was equipped with special jaws for transverse testing. The impact data in the first series of tests were obtained from an impact machine which depends upon the principle of a hammer falling from increasing heights for breaking the sample. In the latter s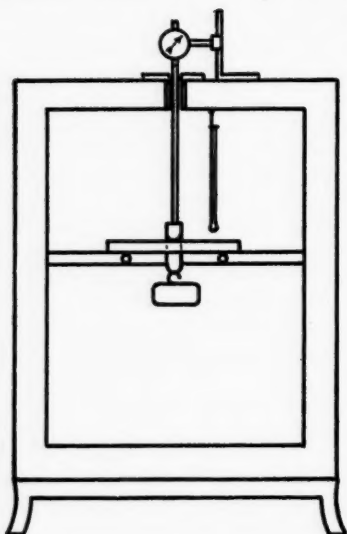eries the impact tests were made on a low capacity pendulum type impact testing machine designed primarily for the examination of insulating materials by W. W. Werring of the Bell Telephone Laboratories.[4] On this machine both the Charpy and Izod methods of testing were carried out. The deformation under heat tests were made in a de Khotinsky electrically heated triple-walled oven. This apparatus was designed after one in the Standards of the American Society for Testing Materials for 1924 and is schematically illustrated in Figure 1.

Methods of Testing

GENERAL—The tests outlined below are modeled after those of the American Society for Testing Materials which are listed under Standard Methods of Testing Molded Insulating Materials.[5]

[3] *Ind. Eng. Chem.*, **18**, 428 (1926).

[4] Proceedings of the American Society for Testing Materials, Part II, 634–680 (1926).

[5] American Society for Testing Materials—Standard Tests on Molded Insulation—D 48-24— and as subsequently revised.

All samples were cut from vulcanized sheet and machined to the dimensions given. All dimensions were measured by micrometers and held within limits of ±0.002 inch. The samples were immersed in water at normal room temperature (68° ± 5° F.) for a period of two hours before testing.
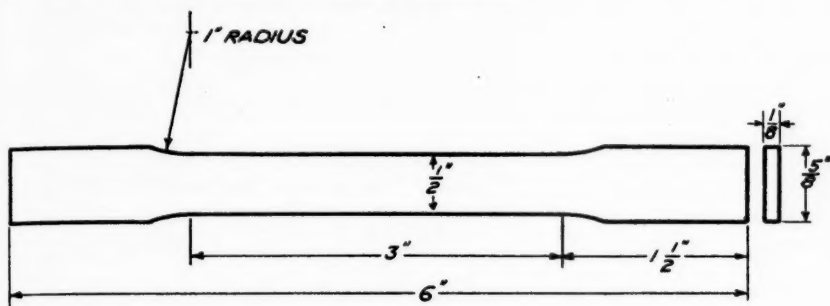
FIG. 2
SAMPLE-TENSILE TEST

In the transverse and tensile tests the cross-head speed of the horizontal machine was 0.4 inch per minute, and of the vertical machine 0.375 inch per minute. The machines are accurate to within 1% of the lowest lead for which they are used.
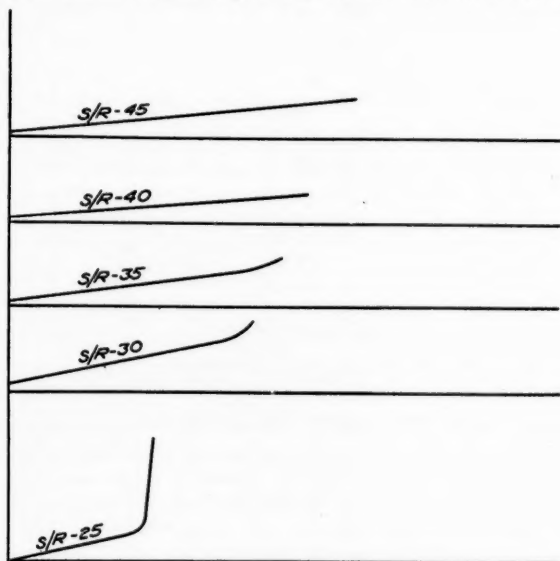
FIG. 3
TENSILE TEST. STRESS-STRAIN CURVES

All results are the averages of at least five tests, except for the softening point tests, which are the averages of two samples.

TENSILE TEST—The samples were machined to the shape and dimension shown

in Figure 2.   In measuring the elongation, marks were made at a distance of 3 inches from each other in the center portion of the sample, and were measured by dividers, which were opened as the elongation increased.   This method is accurate only to $1/_{64}$ in., but is sufficient for showing the variations obtained.   Dial gages connected to the cross-heads of the machine were objectionable, as they measure the distance between the jaws rather than the elongation of the specimen, and, further, they do not take into account slipping in the jaws.

The tensile strength was obtained by dividing the load by the area of the sample. The elongation was expressed in per cent of the three-inch length.   All values were taken at break.

TRANSVERSE TEST—The samples were machined to the dimensions $1/_2 \times 1/_2 \times 6$ inch and were tested on 4-inch centers.   The supports and loading member had
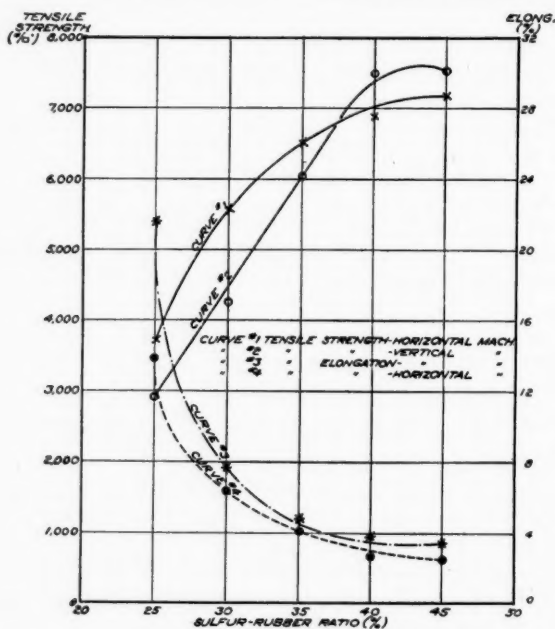
FIG. 4
INFLUENCE OF SULFUR-RUBBER RATIO
ON TENSILE STRENGTH OF HARD RUBBER

rounded contact edges of $1/_8$-inch radii.   The deflection was measured by a standard micrometer of the spring-actuated dial type having a rounded spindle face so that only one point could be in contact with the specimen.   The dial was approximately 2 inches in diameter and was graduated to 0.001 inch.   The pressure of the spindle on the specimen was about 8 ounces.

The transverse strength was figured from the formula for rupture of a simple beam.   The deflection was recorded in inches.   All values were taken at break.

IMPACT TEST—The samples for the falling hammer machine were $1/_2 \times 1/_2 \times 3$ inch and were tested on $1^1/_2$-inch centers.   The first sample was tested starting at a minimum height and increasing this height by $1/_2$-in. intervals to the breaking point.   On the samples after the first, the minimum height was 3 inch below the height of break of the first sample.   For the Charpy test the samples were $1/_2 \times 1/_2 \times 6$ inch with the notch 0.10 inch at the center of the sample and on the side

opposite that to which the blow was delivered; the samples were tested on 4-inch centers.   The Izod samples were $1/2 \times 1/2 \times 3$ inch with a notch 0.10 inch placed $1^1/4$ inch from the top of the sample and on the side to which the blow was delivered. The velocity of impact was 11.4 feet per second.

DEFORMATION UNDER HEAT AND SOFTENING POINT TESTS—The deformation under heat tests were made on samples $1/4 \times 1/2 \times 6$ inch and $1/2 \times 1/2 \times 6$ inch tested on 4-inch centers.   The softening points were determined by the method of Dieterich and Gray,[3] but the tests were made on $1/4 \times 1/2 \times 6$-inch samples supported on 4-inch centers.   The supports and loading member had rounded contact edges of $1/8$-inch radii.   The conditions of these tests in comparison to similar tests made by others are shown in Table I.   The deformation value as stated is the sum of the
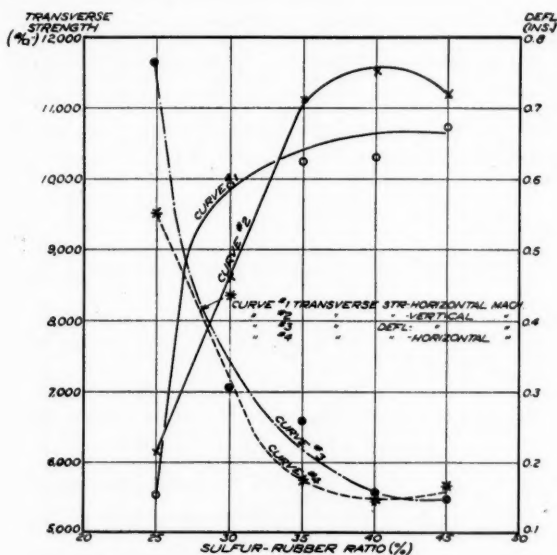
FIG. 5
INFLUENCE OF SULFUR-RUBBER RATIO
ON TRANSVERSE STRENGTH OF HARD RUBBER

initial deflection due to the weight and the deflection due to heating.   This value is not the same as the permanent set and is usually somewhat greater, due to the recovery of the rubber when the weight is removed.   The size of the samples tested and the rate of heating were chosen so that the results of the tests could be obtained in a comparatively short time.

TABLE I
CONDITIONS USED FOR HEAT TESTS

Method	Sample, inches	Distance between supports, inches	Maximum fiber stress, lbs. per sq. in.	Weight, lbs.	Rate of heating
A. S. T. M.	$1/2 \times 1/2 \times 6$	4	264	5.5	1° C./min.
Dieterich and Gray	$1/4 \times 1/2 \times 3$	2	2500	26	2° F./min.
Chosen for Test No. 1	$1/4 \times 1/2 \times 6$	4	1056	5.5	2° F./min.
Chosen for Test No. 2	$1/2 \times 1/2 \times 6$	4	264	5.5	2° F./min.

Note—Constant temperature tests were made at 115° ± 2° F.

Experimental

The formulas of the compounds upon which it was decided to try the tests outlined above are given in Table II. In these formulas, the composition by weight

TABLE II

COMPOSITION OF COMPOUNDS BY WEIGHT

	Compound numbers				
	245	246	247	248	249
Materials			Pounds		
Smoked sheet	15.00	15.00	15.00	15.00	15.00
Reclaimed rubber	30.00	30.00	30.00	30.00	30.00
Sulfur	9.40	11.40	13.20	15.20	17.00
Hard rubber dust	32.75	32.75	32.75	32.75	32.75
Carbon black	2.00	2.00	2.00	2.00	2.00
Light calcined magnesia	0.25	0.25	0.25	0.25	0.25
Pine tar	4.00	4.00	4.00	4.00	4.00
S/R	25.00	30.00	35.00	40.00	45.00

Note—The rubber hydrocarbon content of smoked sheet is taken as 92. The rubber hydrocarbon content of reclaimed rubber is taken as 80. The hard rubber dust is not taken into account in evaluating the sulfur-rubber ratio, as it is supposed to be practically saturated from previous vulcanization.
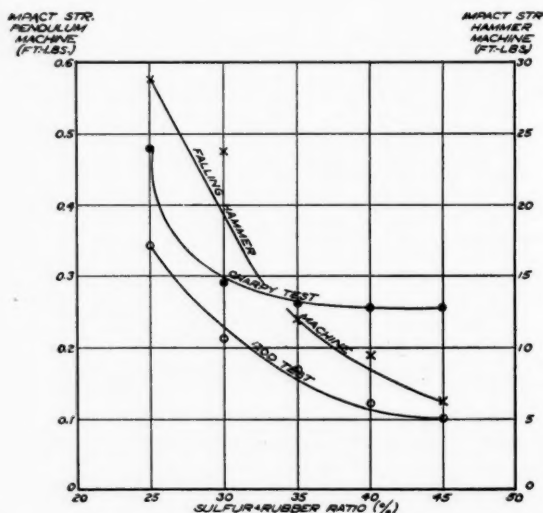
FIG. 6
INFLUENCE OF SULFUR-RUBBER RATIO
ON IMPACT STRENGTH OF HARD RUBBER

of the materials was held constant, with the exception of the sulfur, which was varied to give the sulfur-rubber ratios shown. The compounds were prepared on an experimental mill and calender, plated with tin-foil and vulcanized in open steam for 11 hours at 50 pounds per square inch steam pressure. Partial chemical analyses of the vulcanized rubber and the coefficients of vulcanization are included in Table III. The samples from which the test strips were made were allowed to age at least 72 hours before testing. In the case of the softening point and deformation under heat tests, the samples had aged about two weeks before testing.

TABLE III
FREE SULFUR ANALYSIS AND COEFFICIENT OF VULCANIZATION

Compound number	Approximate S/R	Sulfur in compound, pounds	Free sulfur, pounds	Combined sulfur, pounds	Coefficient of vulcanization	Actual S/R
245	25	9.40	0.09	9.31	24.63	24.87
246	30	11.40	0.11	11.29	29.87	30.15
247	35	13.20	0.13	13.07	34.50	34.92
248	40	15.20	0.27	14.93	39.45	40.21
249	45	17.00	0.43	16.57	44.60	44.97

Note—The coefficient of vulcanization (in %) is taken as the ratio of the combined sulfur to the rubber. The combined sulfur was determined by subtracting the free sulfur as found by analysis from the amount of sulfur added to the compounds.
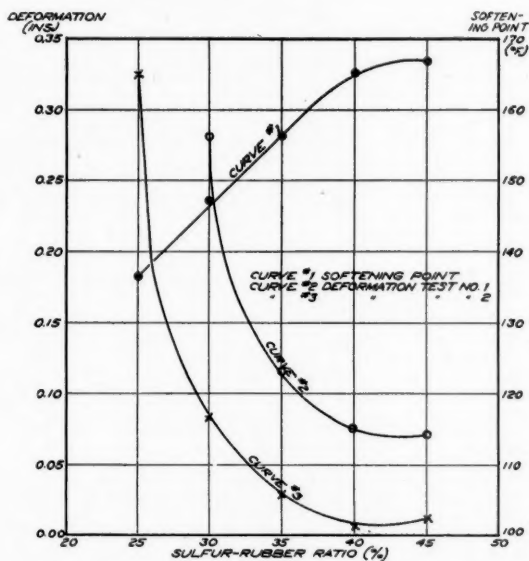
FIG. 7
INFLUENCE OF SULFUR-RUBBER RATIO ON DEFORMATION UNDER HEAT & SOFTENING POINT OF HARD RUBBER

TABLE IV
INFLUENCE OF SULFUR-RUBBER RATIO ON PHYSICAL STRENGTHS OF HARD RUBBER

Sample	Sulfur-rubber ratio	Tensile test				Transverse test				Impact test		
		Hor. machine		Vert. machine		Hor. machine		Vert. machine			Pendulum machine	
		Str. No./ sq. in.	Elong., per cent	Str. No./ sq. in.	Elong., per cent	Str. No./ sq. in.	Defl., per cent	Str. No./ sq. in.	Defl., per cent	Falling hammer, ft. lbs.	Izod, ft. lbs.	Charpy, ft. lbs.
245	25	3686	14.05	2922	21.30	5516	0.550	6095	0.765	28.8	0.34	0.480
246	30	5555	6.25	4205	7.68	9902	0.435	8540	0.316	23.4	0.21	0.293
247	35	6500	4.16	6025	4.30	10300	0.175	11127	0.257	11.9	0.17	0.264
248	40	6885	2.60	7526	3.85	10350	0.145	11535	0.156	9.0	0.12	0.255
249	45	7220	2.50	7511	3.37	10746	0.156	11100	0.150	6.1	0.10	0.255

Results

The stress-strain curves drawn by the attachment of the horizontal machine are given in Figure 3. These curves show especially well the decreasing elongation and

increasing strength which result when the value of the sulfur-rubber ratio is gradually increased. Figure 4 shows the curves obtained by plotting the tensile strength and elongation as ordinates against the sulfur-rubber ratios as abscissae. Figure 5 shows similar curves for transverse strength and deflection; Figure 6 gives curves for the impact strength, while in Figure 7 the deformations under heat and softening points are plotted against the sulfur-rubber ratio. The results of the physical strengths are also given in Table IV, while those of the heat tests are given in Table V.

TABLE V
DEFORMATION UNDER HEAT AND SOFTENING POINT TESTS

		Deformation under heat		
Sample No.	S/R	Test No. 1 $1/4'' \times 1/2''$ samples, inches	Test No. 2 $1/2'' \times 1/2''$ samples, inches	Softening point, ° F.
245	25	. . .[a]	0.327	136.50
246	30	0.282	0.085	147.00
247	35	0.120	0.029	156.50
248	40	0.077	0.009	165.25
249	45	0.072	0.012	167.00

[a] Samples slipped through supports after heating for one-half hour.

Conclusions

1—Investigation of the sulfur-rubber ratio indicates that values below 30 produce rubber whose physical strength is too low and whose flexibility and flow under heat and load are too great for general use. At a sulfur-rubber ratio of 45, the rubber appears to have reached a point where the physical strength is near its maximum value and the deflection is at a minimum. Thus, the compounds having sulfur-rubber ratios between 30 and 45 appear to possess all the properties that are desirable in hard rubber.

2—It is possible to form specifications for hard rubber in which physical tests are used as requirements. Such specifications should be of more value than those which depend upon chemical tests, as they determine the strength of the rubber and the conditions under which it can be best used.

3—Comparable results are obtained in transverse and tensile tests using both the horizontal-pendulum and vertical-floating-beam types of machine; in both cases, however, a more accurate means of measuring the tensile elongation is desirable. In the horizontal machine both cross-heads move so that the speed as stated is somewhat inaccurate; however, the stress-strain diagrams plotted by this machine are advantageous. The tensile strength test appears to give values which can be held within reasonable limits and closely checked. It is believed that when a more accurate means of measuring the tensile elongation is available this result will be of greater value. The transverse deflection is considered more reliable than the transverse strength.

4—In the impact test, better agreement in the results was obtained from the pendulum type machine than from the falling hammer machine. Both the Charpy and Izod methods appear to be suitable. Although there is no agreement between them as to actual values, the curves (Figure 6) show similar trends. The falling hammer test for impact strength is believed to be unsuitable, as is shown by the lack of uniformity in the results.

5—A deformation under heat test, such as Test No. 1, enables one to differentiate between rubbers of varying sulfur-rubber ratios in a comparatively short time. This test appears to be useful as a requirement in specifications on hard rubber.

The softening point tests are not considered as important as the heat-deformation tests, because the temperature to which the rubber will be subjected is usually known and it is desired to find the actual deformation that takes place.

Acknowledgment

The author wishes to express his indebtedness to Dr. E. A. Daniels and H. E. Malone, under whose supervision the major portion of this work was carried out.

Specifications for Rubber Goods and the Value of Performance Tests

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Present specifications, including those of the U. S. Government, the railroads and the cities, are fundamentally wrong, and in spite of elaborate physical and chemical requirements not only fail to assure the purchase of satisfactory goods but actually prevent the purchase of serviceable goods in the most economical manner. The paper is an indictment of specifications of this type, and is well justified because of the recent development of performance tests and of improved methods of compounding, which warrant sweeping changes in specifications. In support of the argument that those who purchase rubber goods by specification are neither aiding nor encouraging physical and chemical developments and are not even taking advantage of what is known, recently developed tests for imitating service conditions, such as abrasion tests, flexing machines and the oxygen-aging test and such adjuncts as reclaimed rubber and antioxidants are discussed, with the inclusion of new data. All of these developments are ignored by the writer of specifications, and at present there is general confusion and extravagance in the purchase of goods. In conclusion a plan is suggested for rectifying the extravagance and ignorance now prevailing.

With the tremendous growth of the rubber industry, it has become of increasing importance to the manufacturer to foresee the behavior of his products in service and to develop tests which duplicate this behavior in a relatively brief time and in a reliable manner. In goods like tires which fail through wear the manufacturer has seen the need of abrasion tests, in goods like bathing caps exposed to sunlight he has appreciated the need of light tests, and in all rubber goods he has realized the value of aging tests. In general there has arisen the necessity of performance tests which foretell the behavior of each of the various types of rubber goods.

Moreover such tests not only enable the manufacturer to foresee the behavior of rubber goods in service, but they also furnish him a means for the study of new methods of compounding and manufacture and thus enable him to improve his products. Most consumers of rubber goods benefit directly by these new tests and by the developments which are going on in the rubber industry, for the public does not purchase its goods by specifications and is interested only in obtaining the most for its money. There are, however, certain large consumers who, with no knowledge of rubber, purchase their goods by rigid and useless specifications.

Even the most important specifications, like those of the United States Government, the railroads, the cities and the fire underwriters, which deal chiefly with mechanical goods, are fundamentally wrong, and in spite of their elaborate requirements, both fail to assure the purchase of satisfactory goods and prevent the purchase at the lowest price of serviceable goods. Rubber goods may be con-

* A description, with photographs, of abrasion machines, as well as the general discussion following the paper, are omitted.

structed to pass specifications and yet fail in service, and, conversely, rubber goods may fail to pass specifications and yet be entirely satisfactory in service, in fact more satisfactory than those which pass the specifications.

This paper deals in a critical manner with specifications, but though the subject is confined to certain important American ones, it is applicable to nearly all others and those of other countries are open to just as severe criticism. Some of the most recently developed tests for duplicating service conditions will also be described, as well as the use of such adjuncts as antioxidants and reclaimed rubber.

Abrasion Tests

One of the most important uses of rubber is in goods which must withstand abrasion, and so there has been considerable effort to develop tests for determining the quality of rubber in this respect.

The mechanism of wearing away the rubber is different on each machine which has been developed, which suggests that relatively different results are obtained on different machines. To establish this point five compounds were tested by seven different methods of wear.

	Tire tread	Conveyor belt cover	Medium grade heel	Low grade heel	Sand blast hose tube
Smoked sheet	60	35	12	...	80
Alkali tire reclaim	6	25	24	24	...
Solid tire oil reclaim	...	...	24	24	...
Sulfur	$2^3/_8$	$1^1/_2$	$1^1/_2$	$1^1/_4$	$2^1/_2$
Ethylideneaniline	$^3/_8$	...	...	...	$^1/_2$
Mercaptobenzothiazole	...	$^1/_4$	...	...	...
Diphenylguanidine	$^1/_2$	...	...	...	...
Phenyltolylguanidine	...	...	$^1/_4$	$^1/_4$	...
Stearic acid	...	$^1/_4$	...	...	...
Pine tar	$^3/_4$	...	2	2	...
Mineral rubber	...	5	8	10	...
Zinc oxide	10	5	...	...	17
Carbon black	20	...	...	...	...
Whiting	...	28	$28^1/_4$	$38^1/_2$	...
	100	100	100	100	100

These compounds were tested on seven abrasion machines, and the resistance to abrasion compared by converting the reciprocals of the rate of wear of each compound on each machine to a basis of 100 for the tire tread compound. In this way the higher the index of a compound shown in the following data, the better its resistance to abrasion, an index below 100 indicating that the compound was poorer than the tire tread compound, and vice versa.

	Tire tread	Conveyor belt cover	Medium grade heel	Low grade heel	Sand blast hose tube
N. J. Zinc Co.					
Quartz track	100	22	29	66	15
Feldspar track	100	18	12	28	13
Intermittent wear	100	26	18	11	54
Akron Std. Mould Co.	100	35	31	27	5500
B. F. Goodrich Co.	100	14	11	7	114
U. S. Rubber	100	39	27	20	38
B. W. H. & R. Co.	100	40	20	9	200

In the Boston Woven Hose & Rubber Co. sand blast machine, a sample of steel gave a value of 7, and a piece of oak was completely destroyed long before the test
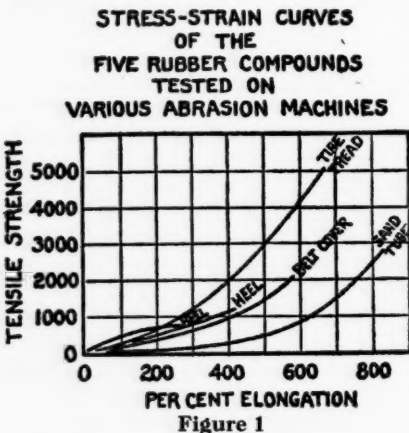
was completed, showing that even the poorest rubber compound containing no new rubber was superior to steel in its resistance to abrasion. A rubber belt was attacked in such a way that the first two plies of cotton duck were eaten out, leaving a sponge-like skeleton of rubber friction.

The stress-strain curves of these same compounds are shown in Figure 1.

The individual abrasion machines indicate the behavior of rubber under different conditions, and the choice of any one of these machines or of any future machine depends upon the type of abrasion which it is desired to imitate. It is unreasonable to expect that a single machine can be designed to duplicate every manner in which rubber undergoes abrasion, and it is preferable to put the utmost skill into the design of a machine which will duplicate one kind of wear, even at the sacrifice of its general utility for such a variety of uses as sand blast hose tubes and tire treads.

There are certain factors in the wear of a tire, notably its hardness, its tendency to tear and a heating effect, which play a part in abrasion, yet which are not well understood, and which therefore must be studied further before an artificial abrasion test can be designed to duplicate road wear. The heating effect plays a greater part than is often realized, for as the tire comes in contact with the road this heating effect often raises the temperature of the rubber to the softening point. This is due to both longitudinal and to transverse slipping of the tire, the transverse slipping being, of course, caused by flexing.

Though the machines in their present state of development are not all that is desired, they represent an important step forward, and they offer a ready means of distinguishing between a compound with high resistance to abrasion and one which wears poorly. To obtain reliable information, one must choose the particular machine which most nearly approaches in its action the actual conditions of wear.

In spite of this, consumers of rubber goods such as conveyor belts are not aiding or even encouraging their development, and are not even taking advantage of them in their present state. The automobile tire companies are more progressive and have carried out road tests on their tires even before the development of abrasion machines, so that they may now compare the performance of various compounds on the road and on abrasion machines.

Flexing Machines

The most important fabric rubber goods which are continually deformed or flexed are pneumatic tires and belting. This flexing tends to cause the plies of fabric to separate.

The test which has been relied upon to determine how a belt will withstand service of this character is the friction test, where either the rate of separation of two adjacent plies under a given tension, or the force required to separate them at a given rate, is measured. This friction test does not distinguish sufficiently between a good belt and a bad one; in fact, a belt having an 18-pound friction has

STRESS-STRAIN CURVES
OF THE
FIVE RUBBER COMPOUNDS
TESTED ON
VARIOUS ABRASION MACHINES

Figure 1

outlasted in service another belt with a 25-pound friction. This is extremely important, for the purchaser may pay a higher price for a high friction test only to obtain a belt which does not last so long as a cheaper belt with a low friction test. Then, again, he may receive two belts showing the same friction test, one of which greatly outwears the other. It is now generally conceded that the friction test is of little value in determining the flexing life of a belt.

A few years ago a machine was developed by the United States Rubber Company which approaches the action of a tire or a belt in service.

It consists of small pulleys over which strips of belting held by clamps pass back and forth. The pulleys are pivoted and the counterweight determines the tension on the strips of tire or belt. Of course, both the stress and the diameter of the pulleys, particularly the latter, govern the number of strokes required to separate the plies, but in any case the action is much more severe than that in a belt in service.

It is not difficult to see why the friction test gives a false indication of the life of a belt and why the flexing test more nearly approaches, even though it does not duplicate, service conditions. At each passage of the belt over the pulley, the

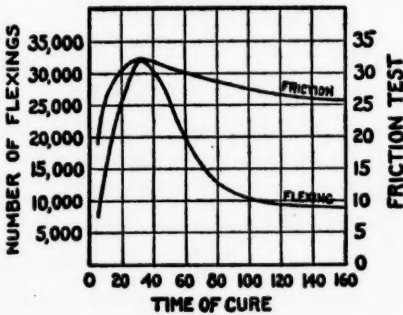CHANGES IN FRICTION TEST AND NUMBER OF FLEXING CYCLES WITH INCREASING CURES

Figure 2

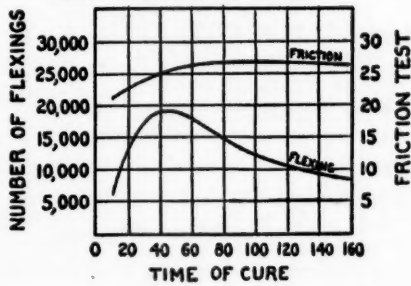CHANGES IN FRICTION TEST AND NUMBER OF FLEXING CYCLES WITH INCREASING CURES

Figure 3

rubber fibers uniting the fabric are stretched and partially recover only to be stretched again. The smaller the pulley the greater this stretch, and the higher the speed and the shorter the belt, the less the time for the rubber to recover before it is stretched again. Therefore the sooner the fibers reach the next pulley the less they have recovered and the higher their residual temperature. The flexing test stretches the rubber much more frequently than a service drive, and so the rubber behaves differently under the two conditions. Therefore two belt compounds may last the same length of time in service, yet break down after different times on a flexing machine, due to the rapidity of the hysteresis cycles. The friction test does not involve repeated stretching and hysteresis losses and so has no relation to service conditions.

Figures 2 and 3 show the changes in the flexing life and in the friction test of two different belts cured for increasing times. In neither case is the friction test nearly so sensitive to over-curing as the flexing life, and there is no relation evident between the friction test and the flexing life of a belt. The curves show clearly that two belts may have the same friction test and yet one far outlast the other in service.

Figure 4 shows that neither the maximum flexing life of the belt nor its friction

test are proportional to the maximum tensile strength nor tensile product. In this graph the tensile product values are expressed as the product of the percentage elongation and tensile strength (in pounds per square inch) divided by 10,000.

Moreover, in service the natural aging of the rubber compound may play an important part. With a tight belt or a belt which has stretched and been shortened, the rubber is under permanent tension, resulting in a rapid deterioration which always occurs when rubber remains under tension. The rubber friction compound may deteriorate so rapidly that in a few months or years it is equivalent to a much poorer compound. Therefore two belts may give the same flexing test, and yet one may give out sooner than the other in service because it contains a compound which deteriorates more rapidly. In this case a flexing test should be combined with an oxygen aging test.

The important question is not whether the flexing test duplicates exactly ordinary service conditions, but whether it is a close enough measure of the quality to warrant its adoption in place of a friction test. The friction test is of little value, whereas the flexing test gives a valuable indication of the behavior of a belt under adverse conditions, information which is of more value to the consumer than its behavior under more favorable conditions. A performance test has therefore been developed which should replace the present unsatisfactory and misleading friction test appearing in most specifications.
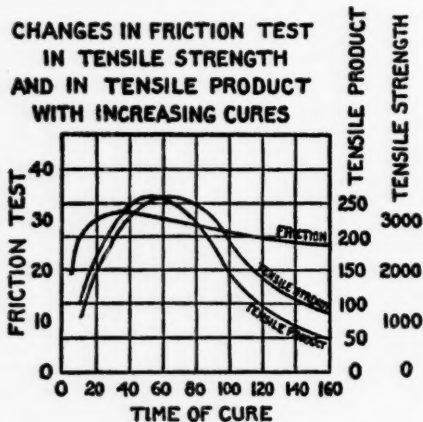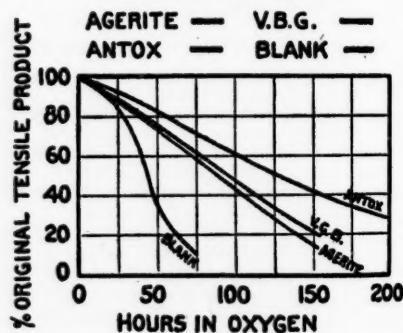
Figure 4

Figure 5

The Oxygen Aging Test

Service tests like abrasion and flexing tests are indispensable for goods which fail in service because of severe mechanical treatment. But there is a wide range of rubber goods which are not treated so severely and which would remain serviceable far longer than they do if it were not for the fact that they oxidize.

The physical changes which accompany this natural deterioration differ with the character of the rubber compound. In some cases the vulcanized rubber compound becomes progressively harder until it finally loses all its elasticity and becomes brittle. Other compounds first become softer and may even become sticky and plastic enough to flow, but in this case also they ultimately become hard, brittle, and resinous.

It has become possible by means of the oxygen aging test (*Ind. Eng. Chem.*, **16**, 711 (1924); **17**, 860 (1925); *India Rubber J.*, **68**, 537 (1924); **70**, 425 (1925)) to

duplicate these different changes, including the changes which occur in rubber cured with sulfur chloride, for tests show that bathing caps which become weak and tacky in storage behave the same way in the oxygen aging test, while better aging caps withstand oxygen correspondingly longer.

There are, however, limitations to the oxygen aging test which cannot be too strongly emphasized.

There are many types of rubber goods which are exposed only a small part of the time or not exposed at all to light, and deteriorate chiefly because of oxidation. It is only this type of natural aging which may be so closely duplicated in the oxygen aging test. Some rubber goods not only undergo atmospheric oxidation, but are exposed to sunlight and to heat. When rubber shoes and automobile toppings are exposed to light, they deteriorate much faster and crack much sooner than when stored in darkness. Steam hose deteriorates from heating, and natural aging plays little or no part. To duplicate these conditions exactly would require a test which combines the action of light, oxygen, heat, and humidity in such a manner that the relative intensities of these factors would agree with the particular conditions encountered in natural aging.

An artificial test might be devised in which the rubber is exposed simultaneously or in repeated cycles to ultra-violet light, to oxygen, to a temperature above normal and to the proper humidity so that the various conditions causing deterioration under natural conditions would be intensified to the same degree.

Investigation of various conditions and experience with a wide variety of compounds subjected to oxygen at different pressures and temperatures has shown that a pressure of oxygen of 300 pounds per square inch at 60° or 70° C. brings about in a reasonable number of hours a deterioration similar to several years of natural aging in darkness. Since this type of aging at ordinary temperatures is chiefly oxidation, the rate of this deterioration depends upon the temperature. In fact, on the basis of a chemical reaction, rubber goods should deteriorate about twice as fast at 25° C. as they do at 15° C., and therefore it is impossible to specify that a definite number of hours in oxygen gives the same result as one year of natural aging, since the temperature of the natural aging may vary considerably.

It is often preferable to carry out an oxygen aging test at 70° C. instead of the more frequent 60° C., particularly where very resistant compounds are involved, which prolong the time of testing at 60° C. beyond a convenient limit.

Owing to the facility and reliability with which natural aging at ordinary temperatures and in darkness may be practically duplicated, the oxygen aging test has grown from a small beginning in 1923, to a point where seventy-four American companies are using the test. Close duplication in a few hours of several years of natural aging renders the determination of the aging properties of vulcanized rubber compounds very easy. Formulas and compounding ingredients whose aging properties are unknown can be investigated in a very brief time.

Two actual examples will show the value of the oxygen aging test.

Having developed a new inner tube, a large American company found discordant results between the 70° C. air oven test (*India Rubber World*, **55**, 127 (1916); *India Rubber J.*, **61**, 1163 (1920)) and the oxygen aging test. The oven test indicated an excellent compound, while the oxygen aging test gave warning that the inner tubes would deteriorate badly. Trusting the more favorable oven test, the inner tubes were sold, and within one year $150,000 worth were returned because of bad aging, exactly as predicted by the oxygen aging test.

Another American company supplying inner tubes to busses on the Pacific Coast received complaint that the tubes became soft and tacky after 5000 miles. Other inner tubes were tested in service, and it was found that the best inner tube, judged

by the oven test, was the worst on the road. Resort was then had to the oxygen aging test, and by its aid the company was able to develop inner tubes which are still in good condition after running 20,000 miles.

Antioxidants and Improvements in the Aging Properties of Rubber

Among the factors contributing to the deterioration of vulcanized rubber, the most serious are light, heat, and oxygen. Therefore if rubber were protected from all three influences, its life would be greatly prolonged. It may be protected from light to some extent by proper compounding or by storing it in darkness. It may be made resistant to heat only by proper compounding and the results which can be obtained in this respect are remarkable. Thus a compound cured with an alkyl thiuramdisulfide in the absence of sulfur shows a surprising resistance to the action of heat or to prolonged over-curing. The following compound containing tetramethylthiuramdisulfide:

Smoked sheets	100
Tetramethylthiuramdisulfide	2
Zinc oxide	10
Carbon black	25

was vulcanized one-half hour, one hour, and eight hours at 142° C. in a press, with the following results, the data giving the percentage elongation at break and the tensile strength in pounds per square inch, respectively, before and after aging 48 hours in oxygen at 70° C. and 300 pounds per square inch pressure:

	Original tests		After aging	
Cure	Elongation	Tensile strength	Elongation	Tensile strength
$^1/_2$ hr.	650	3070	570	2080
1 hr.	620	3050	550	2000
8 hrs.	600	2920	490	1540

In its resistance to prolonged heating, this compound is far superior to a similar compound containing sulfur and a less active accelerator, and it also has satisfactory aging properties.

The influence of atmospheric oxygen, the third factor, is often the most serious, but fortunately the easiest to combat. This is a statement which could not have been made fifteen years ago, but which the development of organic accelerators and of antioxidants has made an undisputed fact. Organic accelerators not only increase the economy of curing and improve the properties of cured rubber, but also improve the aging of rubber and increase the range of cure over which the rubber ages well. But another class of substances, called antioxidants, far exceeds organic accelerators in their ability to improve the aging of cured rubber. These antioxidants are, in general, substances which, under proper conditions, retard the oxidation of much larger quantities of other substances, though the mechanism of their action is still a matter of speculation.

Since both organic accelerators and antioxidants improve the aging properties of cured rubber, antioxidants are from one point of view not new, for when organic accelerators were developed antioxidants also came into use without our fully appreciating the fact. Neither the mechanism of acceleration nor the action of antioxidants is known, and it is possible that many accelerators and antioxidants have certain properties in common. From this point of view accelerators are relatively powerful in their accelerating action and relatively weak antioxidants, while many antioxidants are relatively weak accelerators and relatively powerful in their antioxidizing action. A sharp distinction cannot be drawn between many

accelerators and antioxidants, and they must be judged only by their predominant characteristic. This is further complicated by the fact that some antioxidants even retard the rate of vulcanization.

Though the influence of antioxidants on rubber and the development of new antioxidants have been studied within the rubber industry, the impetus for this development must be credited to Professor Moureu at the Collège de France, who in a series of masterly researches has shown that many compounds, particularly phenols, when present even in extremely small quantity, inhibit the oxidation of many organic compounds, including oils, resins, rubber, and many technically important substances. The essentially academic researches of Moureu, which, however, led him to obtain patents for retarding the oxidation of oils, resins, rubber, etc., have been followed by the development of antioxidants with a specific action on rubber. This is a striking example of the prompt utilization and commercial application of what was at first purely academic organic chemical research. At present intensive research is being carried on to find more powerful antioxidants among compounds already known and to synthesize new compounds of greater antioxidant power. Meanwhile their use is growing, and over 250 tons are used each month in the United States alone.

Three substances have attained commercial importance in the United States, (1) *Agerite*, which is aldol-α-naphthylamine, (2) *V. G. B.*, a condensation product of acetaldehyde and anilinehydrochloride, and (3) *Antox*, a mixture of para-aminophenol and barium sulfate. There will doubtless be far superior antioxidants developed which will displace these three, just as superior accelerators were developed to replace the earliest ones which were considered so remarkable.

The effects of antioxidants on the aging of an accelerated compound may be illustrated by the following tests, in which the base compound:

Smoked sheets	100
Sulfur	4
Diphenylguanidine	$^1/_2$
Zinc oxide	4
Precipitated whiting	50

was cured for 20, 30, 40, 60 and 90 min. at 142° C. in a press, with and without the addition of $^1/_2$, 1, $1^1/_2$, 2, and 3 parts of *Agerite*, *Antox*, *V. G. B.*, and *Nonox*, the last named an antioxidant produced in England. The various cured compounds were then aged in oxygen under 300 pounds per square inch pressure at 70° C. for various lengths of time. The results, enough of which are given to show the general effect of the antioxidants, are expressed as the decline of the tensile product as aging progressed. The tensile product of each compound was considered to be 100 per cent when new, and the deterioration is shown simply as a decreasing percentage of the original value. The compounds were vulcanized with diphenylguanidine because, unlike some accelerators, this one has no antioxidant properties of its own. In the data shown, only the best aging cures of the individual compounds are included.

Figure 5 shows the deterioration with 1 per cent of antioxidant, Figure 6 with $1^1/_2$ per cent, Figure 7 with 2 per cent and Figure 8 with 3 per cent.

Figure 9 shows the effect of over-cures on the aging of the compounds with antioxidants, in comparison with the best aging cure of the compound containing no antioxidant.

Only one antioxidant is shown, but all those mentioned behave in the same manner, in that they fail to protect a badly over-cured compound from comparatively rapid deterioration.

The results are sufficient to indicate several facts, the most important of which are:

(1) That in small quantities one antioxidant may be considerably more powerful than another, whereas in larger quantities the two become approximately the same in their action, and (2) that even when a compound contains an antioxidant, its

AGING IN OXYGEN 300 LBS. PRESSURE 70°C

1½% ANTIOXIDANT

AGERITE —— V.G.B. ——
ANTOX —— BLANK ——
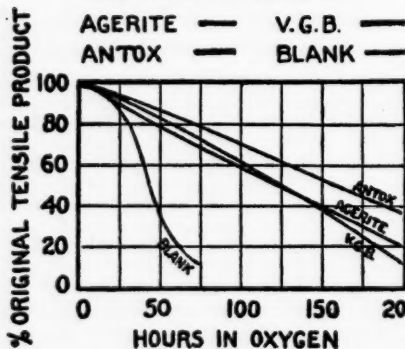
Figure 6

AGING IN OXYGEN 300 LBS. PRESSURE 70°C

2% ANTIOXIDANT

AGERITE —— NONOX ——
ANTOX —— V.G.B. ——
BLANK ——
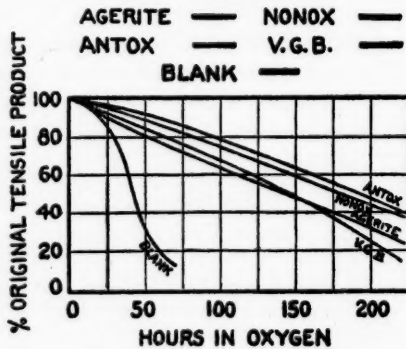
Figure 7

deterioration may be comparatively rapid when it is over-cured. This latter fact is contrary to a widespread belief that antioxidants are particularly effective retarding deterioration in a badly over-cured compound.

The data deal with but one base compound, and are given merely to illustrate some characteristics of antioxidants and to show that the choice of a particular antioxidant in a compound must be determined by actual tests. If, for instance,

AGING IN OXYGEN 300 LBS. PRESSURE 70°C

3% ANTIOXIDANT

AGERITE —— V.G.B. ——
ANTOX —— BLANK ——
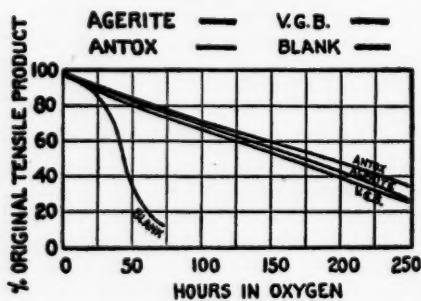
Figure 8

EFFECT OF OVERCURE
ON AGING OF A COMPOUND
WITH AN ANTIOXIDANT

1½% ANTOX
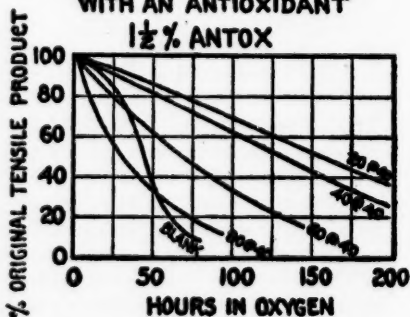
Figure 9

mercaptobenzothiazole had been used instead of diphenylguanidine, considerably different results would have been obtained, for the former accelerator is also an antioxidant.

By the aid of antioxidants, it has become for the first time possible to retard the rapid deterioration caused by a copper compound. This may be illustrated by the

following three compounds, the first containing no copper salt or antioxidant, the second containing cuprous iodide, and the third both the copper salt and an antioxidant. Here, again, diphenylguanidine was used, for it has no protective action itself. The data give the ultimate elongation (percentage) and the tensile strength (pounds per square inch) when new and after ten months of natural aging.

|				
	Smoked sheets	100	100	100
	Sulfur	4	4	4
	Diphenylguanidine	0.5	0.5	0.5
	Zinc oxide	4	4	4
	Whiting	50	50	50
	Cuprous iodide	....	0.3	0.3
	Antox	....	....	1.5
When new	{ Elongation	650	660	650
	{ Tensile strength	3580	3550	3600
After 10 months	{ Elongation	620	80	630
	{ Tensile strength	3490	250	3510

After ten months the base compound containing cuprous iodide was badly deteriorated, while that containing both cuprous iodide and *Antox* was as good as the compound containing neither one. There are, however, antioxidants which are even better than *Antox* in the absence of copper compounds, but which fail to protect the rubber when copper compounds are present. There are other antioxidants which are very effective in prolonging the life of cured rubber compounds containing copper compounds.

Antioxidants have become firmly established in rubber compounding, for they enable the manufacturer to prolong the life of his rubber products and to guard against errors in compounding, impure ingredients, and variations of manufacture. Their use is therefore a valuable insurance against bad aging.

The foregoing discussion is sufficient to show that performance tests are already at the disposal of the consumer, and in what follows it will be shown such tests are urgently needed.

The Character of Present Specifications

Considering that seventy-five per cent of all rubber is consumed in the manufacture of automobile tires and that most rubber goods are purchased by those having little interest in their manufacture or construction, it is obvious that the purchase of rubber products by specifications is restricted to relatively few consumers. Owing, however, to the importance of such goods, specifications play a very important part in the rubber industry, particularly mechanical rubber goods.

There are two general types of specifications which guarantee the consumer serviceable rubber goods. The first type deals in complete detail with the quality of the raw materials which make up the finished goods and with the construction of these goods, and then requires performance tests as a further safeguard. The second type limits itself to performance tests, and is based on the principle that as long as the goods give satisfactory service, their construction should be left to the manufacturer.

To be satisfactory either to the manufacturer or to the consumer, the first type must be written by an expert familiar both with the details of manufacture and with the behavior of the goods in service. Such knowledge is obviously beyond the scope of nearly all consumers, and therefore the second type of specification, that dealing with performance tests alone, is the only type which the consumer is in a position to write. In spite of this, consumers write nondescript specifications which restrict the manufacturer to the production of uneconomical goods which are faulty in construction and which behave badly in service.

In spite of a tendency to copy one another's specifications and in a few cases to use a common specification, there have been no essential improvements in recent years, and specifications are more faulty today than twenty years ago. At that time they guaranteed the consumer as high a quality as it was possible to obtain, but they have remained still fundamentally the same and at present they restrict the manufacturer to such an extent that he cannot give the consumer the benefit of the tremendous improvements in the art of rubber manufacture. The day has in fact come when specifications actually prevent the purchase of the most economical and most satisfactory goods. Millions of dollars worth of rubber goods are purchased annually to specifications which base their requirements on the quality and the behavior of vulcanized rubber of twenty years ago, when organic accelerators and antioxidants were unheard of, when carbon black had never been used, and when abrasion machines, aging tests, and other means of duplicating service conditions were unknown.

A good word must, however, be said for a few organizations. The American Telephone and Telegraph Company has excellent specifications and an inspection department which is progressive and willing to adopt new developments as a means of purchasing rubber goods, and its frequent publications on the science of rubber bear witness to the contributions which can be made by an intelligent consumer. The specifications of the National Board of Fire Underwriters are as objectionable as most others, but this organization has inspectors who work on an equitable basis, a compliment which cannot be paid to the inspectors of the unskilled laborer type so prevalent among most inspection organizations.

Specifications have become so absurd that rubber goods may actually be rejected because they do not deteriorate. One of the largest railroad systems in America requires that the tube of its steam hose shall, when new, elongate between 200 and 400 per cent at rupture. After digesting 48 hours in steam at 45 pounds per square inch, the tube must elongate between 100 and 300 per cent. The best hose possible to manufacture, which does not deteriorate at all during steaming, has been rejected because the tube elongated 375 per cent before and after steaming. It would almost appear that the specification department of this railroad desires poor steam hose, and their inspection department leaves little undone to prevent the acceptance of good steam hose.

Misused Tests in Specifications

Among requirements which cause tremendous waste of money to the purchaser are maximum and minimum elongation and tensile strength tests, permanent set tests, oven tests, a minimum rubber content, forbidding the use of reclaimed rubber, a maximum combined and free sulfur, maximum acetone, chloroform, and alcoholic caustic alkali extracts, a maximum and minimum ash content and various other unnecessary tests, many of which apply to the construction of the rubber goods. Space allows a discussion of only a few of these irrelevant tests.

In requiring a high elongation and tensile strength in a hose tube and cover, the consumer ignores the fact that the rubber is never elongated to any considerable extent nor subjected to any high stress, and he seems not to realize that it is far more important to know whether after a year or two the tube bends without cracking and the cover is not cracked from exposure to air and sunshine. In present specifications, elongation and strength tests not only fail to assure the purchaser of the quality he desires, but usually necessitate his paying higher prices. It would be better to require an elongation of 350 per cent and a tensile strength of 1000 pounds per square inch, and then allow only 20 per cent deterioration in 2 years than to require 500 per cent elongation and a tensile strength of 1600 pounds per square inch and then ignore the aging.

Specifications frequently include a test for permanent set. The American Railway Association requires the tube and cover of air-brake hose to be stretched 400 per cent, immediately released, immediately stretched again 400 per cent of its new length, held 10 minutes at this strain and released. Within 30 seconds after this final release, the length must be not over $12^1/_2$ per cent greater than it was previous to the final stretching and after 10 minutes must be not over $6^1/_4$ per cent greater. A rubber technologist can see no relation between this elaborate test and the behavior of the cover when exposed to sunshine and air.

Manufacturers meet this test by curing their hose to a point which makes it impossible for the hose to age well, and there have been tens of millions of feet of air-brake hose manufactured in the United States which have been over-cured simply to obtain the permanent set required in the specification. As a result the hose has deteriorated more rapidly than the cost and type of compounds warrant, and most hose is removed from service because of the cover cracking and not because the hose has become unserviceable in any other way. This may seem an astounding fact, but it was verified in a recent examination of air-brake hose.

Engineers of tests of four large American railroads on being questioned were found to be entirely ignorant of the manner in which their own air-brake hose failed in service and why it was removed. Accordingly 11,000 lengths of air-brake hose which had been removed from service were purchased by an American rubber manufacturer. Each length was examined and classified by manufacturer, by railroad, and by cause of removal from service. The lot contained hose manufactured by every manufacturer of air-brake hose in the United States, and used by 38 different railroads, so that the lot was an excellent criterion of what happens to air-brake hose in service and why it is removed. Only 11 per cent had been removed because of bursting, 2 per cent for defects of manufacture, 14 per cent because of injuries, and 73 per cent because there were cracks in the cover and only for that reason.

When railroads remove three-quarters of their air-brake hose because the cover cracks while the hose is otherwise in excellent condition, two points are obvious, that they are unpardonably extravagant in their methods of discarding hose, and that their hose specification is fundamentally wrong.

To justify the latter criticism, air-brake hose was constructed in a manner identical to that regularly accepted by railroads, except that in place of the regular expensive cover, a cover costing only 38 per cent of the regular grade was used. Both the regular hose and this cheaper grade were exposed with a right angle bend outdoors to the elements and were examined periodically. At the end of five weeks the cover of the hose acceptable to the railroads was badly cracked, while the hose with a cover costing only 38 per cent of the above was in good condition at the end of one year.

Chemical Tests

Chemical tests originated in the earlier days when every softener and every low grade rubber were assumed to be injurious, but even at the present time chemical tests of the most unreasonable kind frequently appear.

The most important specifications with chemical tests are those of fire hose. The specification of the National Board of Fire Underwriters requires that fire hose shall contain not over 4 per cent total acetone extract, not over 2 per cent chloroform extract after the acetone extraction, not over $1^1/_2$ per cent alcoholic potash extract after the chloroform extract, not over 4 per cent total sulfur, not over $1^1/_4$ per cent free sulfur, between 50 and 57 per cent ash, and the sum of all these except the free sulfur not over 67 per cent.

Nevertheless a fire hose tube has been made which purposely violates these chemical requirements individually and collectively and yet makes better fire hose. This is illustrated by the following fire hose compounds.

The first tube (A) shown below is characteristic of hose used for many years by some of the largest of the fire hose manufacturers and it passed the chemical tests in every detail. The second tube (B) could not be used in the National Fire Underwriters' specification hose because it violates every chemical test. Tests of actual fire hose constructed with these tubes are given below, the data representing the per cent ultimate elongation and the tensile strength in pounds per square inch.

A		B	
Smoked sheets	44	Smoked sheets	35
Sulfur	2	Tire caustic reclaim	10
Litharge	10	Sulfur	$2^{1}/_{4}$
Zinc oxide	30	Ethylideneaniline	$^{3}/_{8}$
Whiting	14	White substitute	2
	—	Mineral rubber	10
	100	Zinc oxide	20
		Lithopone	$20^{3}/_{8}$
			—
			100

			A	B
When new	{	Elongation	580	620
	{	Tensile strength	2590	2440
After 2 yrs.	{	Elongation	420	570
	{	Tensile strength	1640	2160
After 4 yrs.	{	Elongation	150	460
	{	Tensile strength	940	1730

The aging of the compound containing reclaimed rubber and without the uneconomical litharge is much superior to that of the litharge compound, and could have been rendered still better by the use of an antioxidant.

This example is typical of many where it is advantageous to purchase rubber goods which violate specifications. They are usually better in quality and more economical.

The purchaser wastes tremendous sums of money when he requires that his rubber goods shall contain a minimum percentage of rubber. The United States Government, a notable offender, requires of some of its goods a minimum of 75 per cent rubber by volume, with no specific reference to other ingredients. Provided a compound contains at least 75 per cent by volume of rubber, it may contain a large amount of litharge, be badly over-cured and deteriorate rapidly, yet be perfectly acceptable. On the other hand, a compound more scientifically compounded, with an organic accelerator, with carbon black to increase its resilient energy, with an antioxidant to increase its span of life and with better physical properties before and after aging, will be rejected because it contains only 68 per cent rubber.

Piano tubing represents a negligible expenditure in a piano. No expense is spared to install the finest tubing possible, tubing which must remain in good condition for ten, fifteen, or even twenty years. Not only is this thin-walled tubing exposed to air and continually being flexed, but its ends are in that condition most disastrous to rubber, in that they are stretched under tension over brass pipes. Its service thus resembles that of fire hose in that each is bent, each is distorted at the ends and each is exposed for years to air in darkness. The most resistant and longest lived compound which has yet been developed for piano tubing is one which contains only $27^{1}/_{2}$ per cent rubber by weight. This compound will last for many years without cracking, and, though lasting four times as long as most fire hose, costs only three-quarters as much as the rubber tube in fire hose. It might be

well to add that piano manufacturers are more progressive and far-sighted than railroads and fire hose consumers and purchase piano tubing by performance tests.

Railroads, cities, and national governments can only purchase hose in the same way as piano manufacturers if they are alive to developments in the rubber industry and are willing to coöperate with the manufacturer in devising specifications which apply the most advanced knowledge of rubber technology to the construction of serviceable, economical rubber goods. This, of course, means a capable technical staff, which the present consumers in very few cases have.

Reclaimed Rubber

Nearly all specifications dealing with the highest quality of rubber goods prohibit the use of reclaimed rubber. This unnecessary restriction means so much from an economic point of view that it deserves special comment. At one time it was generally thought that reclaimed rubber, though very useful in cheap rubber compounds, was disastrous in high-grade ones, and that when the latter contained even a small proportion of reclaimed rubber they were poorer than similar compounds containing none. It has, however, been proved in recent years by rubber technologists that the judicious use of reclaimed rubber in high-grade compounds does not impair the quality, and the writers have recently published quantitative data (*Ind. Eng. Chem.*, **18,** 348 (1926); *India Rubber J.*, **71,** 565 (1926)) to show that the use of reclaimed rubber allows the production of rubber products which are of as good quality and which age as well as similar compounds containing only new rubber, and at times are of better quality than those containing no reclaimed rubber. These laboratory tests of tire tread compounds have since been confirmed by road tests, so that there is no longer any doubt of the advantage of reclaimed rubber.

Reclaimed rubber was not used in increased quantities during the past two years in retaliation for the high price of rubber, but because the unusual price of rubber awoke the more backward manufacturers to the advantages of reclaimed rubber. Tires in America are running farther than ever before, and the fact that they contain reclaimed rubber means that the latter has become established as a beneficial ingredient in rubber compounds subjected to the most severe wear. It is not to be expected that the same quality will be maintained if part of the new rubber is replaced by the same weight of reclaimed rubber. On the other hand, partial replacement of new rubber by a larger quantity of reclaimed rubber, with proper alterations of the other ingredients, does not impair the quality for many uses. Of course, the quality of reclaimed rubber governs the quantity which may be used, but in compounds such as tire treads the resistance to abrasion is not impaired when as high as ten per cent of new rubber is replaced by the proper quantity of reclaimed rubber.

This fact becomes of profound significance in its relation to the rubber market, for by using sufficient reclaimed rubber, the supply of new rubber is conserved, and its price thereby maintained at a reasonable figure. Let it be emphasized that fluctuations in the price of rubber are of no advantage to the plantations, to the manufacturer of rubber goods, or to the consumer. By way of digression, it might also be mentioned that the planters are worthy of great praise. They have created a supply of an extraordinarily valuable product, and have at the same time tremendously improved it commercially, so that they should receive great credit for the present dominant position of the rubber industry. The benefit which the entire civilized world derives from their initiative and ability will be increased by an intelligent coöperation between rubber producer, manufacturer, and consumer, and one of the facts which must be recognized by the rubber grower as well as the consumer is the inherent value of reclaimed rubber.

The question is therefore no longer whether reclaimed rubber is a desirable ingredient in tires and other products, but why it is beneficial, why it may even increase the resistance to abrasion.

One explanation of this increase may be illustrated by analogy. A paste of zinc oxide or other pigment is made with kerosene, turpentine, xylene, or other suitable liquid, so that the paste can be kneaded without either flowing or crumbling. A very small proportion (2 per cent by weight of the zinc oxide) of acetone extract of reclaimed rubber is added to the paste, whereupon by rubbing the latter immediately becomes thin enough to pour.

It is possible that there are substances in reclaimed rubber which have a very powerful dispersing action in this way, and therefore the addition of reclaimed rubber to a high-grade compound wets the pigments better, increases their dispersion, and thus improves the quality of the compound.

Each powder requires a different quantity of liquid to make a paste, but an indication may be had by the fact that 10 grams of zinc oxide, carbon black, whiting, barytes, and china clay require in the neighborhood of 10, 25, 6, 2, and 10 cc., respectively, of kerosene to make a suitable paste.

A zinc oxide–kerosene paste may also be "liquefied" by similar small quantities of the acetone extract of raw rubber, degras, palm oil, oleic acid, stearic acid, rosin, pine tar, liquid asphalt, "Agerite," *V. G. B.*, and numerous other agents. A particularly large number of agents "liquefy" zinc oxide pastes, but pastes of other materials, particularly carbon black, are much less readily "liquefied."

Degras and especially the accelerator "Trimene" have a thinning action on a carbon black–kerosene paste, while one of the most striking cases is the "liquefaction" of a carbon black–water paste by sodium oleate, a carbon black–water (2:5) paste being "liquefied" by 8 per cent sodium oleate on the weight of carbon black.

There is a minimum proportion of thinning agent to pigment below which "liquefaction" does not take place. This minimum varies with each combination, and is, for example, only about 0.3 per cent with stearic acid or oleic acid by weight of zinc oxide. This minimum is, moreover, practically independent of the particular liquid and its proportion used in making the paste. It is possible by a suitable thinning agent to "liquefy" pastes of any of the ordinary rubber compounding ingredients such as carbon black, zinc oxide, whiting, clay, lithopone, slate, barytes, magnesium carbonate, lime, litharge, red iron oxide, etc.

The reason for dealing at such length with the subject of reclaimed rubber is because of its importance in connection with specifications. There are many rubber compounds, in fact, nearly all those used in specification goods, where the desired quality can be obtained either by new rubber alone or by a mixture of new and reclaimed rubber. Specifications which prohibit reclaimed rubber of any kind under any conditions make impossible the production of specification goods in the most economical manner. Since rubber goods containing reclaimed rubber will meet all service conditions in just as satisfactory a manner as goods containing a new rubber alone, and at a lower cost, it is indeed unfortunate that large consumers, such as the United States Government, fail to recognize the proper place of reclaimed rubber in specification goods.

The Outlook for Improvements

In the preceding discussion a great deal of space has been devoted to air-brake and fire hose specifications. These were selected not because they are exceptionally bad, but because they are used so extensively and because so many people are familiar with them. To appreciate to the fullest extent the loss caused by these specifications, the following facts are presented.

American consumers purchase $2,200,000 worth of fire hose each year by specifications. This hose could be manufactured for ten per cent less cost and yet contain rubber compounds which would last twice as long. The annual saving would probably be at least $750,000.

Air-brake hose is purchased in 22-inch lengths, having a rubber "cap" on each end and intended to protect the duck. Steam hose for heating cars and used in the same location is purchased in 24-inch lengths, but with raw ends, yet there is no complaint of injury to the duck in service. If rubber caps are unnecessary on steam hose, they are unnecessary on air-brake hose, and yet the railroads of America pay 8 per cent more, i. e., $236,000 per year, for this useless item.

The railroads of America purchased $2,950,000 worth of air-brake hose in 1926. If their specifications had not prevented it, a more properly balanced type of hose giving better service and aging far better could have been manufactured at so much lower cost that the railroads would have saved at least $1,500,000 the past year.

This same air-brake hose now costs 15 per cent more than it did in 1914, and yet it is of the same quality. On the other hand, automobile tires cost only 40 per cent as much as they did in 1914, but have improved so much that they give three times the service. Therefore the railroads, with their self-satisfied specification engineers and inspectors, are receiving 15 per cent less for their money than they did in 1914, while the consumer of tires, who has placed his faith in the manufacturer, is receiving $7^1/_2$ times as much as he did in 1914.

The savings which could be made on other specification goods are proportionately large, and it is conservatively estimated that consumers who purchase mechanical rubber goods by specifications are paying 50 per cent more for the service which they receive than the consumers who are deriving the benefit of developments in the art of rubber manufacture and purchase their goods on a basis of the service rendered.

The purchase of rubber goods by specifications at the present day is faulty in two respects: first, because the specifications themselves are fundamentally wrong in the materials and construction which they require, and, secondly, because the specification and inspection departments of the consumers are too unfamiliar with rubber and too autocratic to interpret liberally any type of specification. Where specifications should be solely a means to an end, they are regarded at present as an end in themselves, and the fact that they fail in their object—i. e., the purchase of the most economical goods in service—is sufficient evidence that they are fundamentally wrong.

The need of performance tests is obvious, but if such tests are merely added to present specifications the situation will be aggravated, for the consumer will continue to pay a premium for his inferior goods and will doubtless misuse and misinterpret performance tests as he does his present tests. There is little hope of specifications being revised until the executives who control the specification and inspection departments insist upon having a personnel with technical training in the performance of rubber goods, and with more interest in obtaining economical goods.

The present misuse of specifications is not only highly regrettable, but is also inexcusable, and is directly chargeable to three guilty parties. In the order in which they must share this guilt stand the manufacturers, the specification departments of the consumers, and the higher executives over these departments.

Manufacturers of mechanical rubber goods have known for a long time that specifications were defeating their purpose, and they have been guilty as a group in not presenting this fact in a forcible manner to the executives of the organizations using these goods, more particularly the high executives of the various railroads. It is obvious that these executives do not knowingly pay extra money for inferior goods, that they believe in dealing in an equitable manner with those from whom

they purchase, and if they were aware of the present situation they would unquestionably remedy many of the existing evils.

The manufacturers have been guilty from another point of view, in that they have continued to sell goods by specifications which they know are faulty, and have tolerated inspection departments which refuse to work on an equitable basis. This toleration has been encouraged by the short-sightedness of certain manufacturers who feel that if they do not furnish the goods requested, some other manufacturer will do so. This reasoning is unsound, because if a few prominent manufacturers were to adopt a firmer attitude toward these absurd specifications, the situation would soon improve.

The principal charge against the specification and inspection departments of the consumers is that they know little or nothing about the manufacture of mechanical rubber goods and their behavior in service. This lack of knowledge is not surprising when it is considered that rubber is only a very small part of their purchases and that they cannot be experts in everything. They are, however, unfair to their own organizations and unfair to the rubber industry when they write specifications on a subject about which they know little and in which the art of manufacture is developing too rapidly for them to follow. There is a reason for their lack of knowledge, but there is no excuse for their autocratic attitude.

The guilt which the higher executives of the consumers share in the present situation is only indirect, and is merely a result of their having subordinates far removed who have been given authority much beyond their knowledge and ability. These executives are ever ready to correct any bad condition if they are informed of the facts.

Consumers in general can purchase rubber goods more economically than at present by completely reorganizing both their requirements and their methods. Their present requirements have already been discussed at sufficient length to show the need of complete revision, and their methods have also been shown to be inefficient and at times unreasonable.

It is possible for large consumers of mechanical rubber goods, who are now purchasing by specifications, to buy their goods in a strictly economical manner, and one possible solution of their problem is offered in the form of a concrete suggestion for the largest consumer of all. The latter comprises the members of the American Railway Association, and it would be easily possible for them to reorganize and establish a centralized specification and inspection department. This would be headed by a highly trained personnel with an intimate knowledge of the manufacture and behavior of rubber goods. This organization would serve all members of the Association, and only an organization of this character can keep up to date and enable its members to benefit by the improvements in rubber manufacture which are continually appearing. The central department would have branches at the important centers of rubber manufacture, and would have trained inspection staffs to examine goods at their place of manufacture.

With a centralized organization under proper control, the consumer would be able to purchase better goods for less money, to receive his goods more quickly, to reduce the cost of his inspection, and finally to benefit promptly by the continual improvements in the art of rubber manufacture.

Acknowledgment

Methods for the Purification of Rubber Hydrocarbons[1]

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The various methods which have been used for preparing the rubber hydrocarbon in a pure state are discussed critically. The authors show that Harries' method of acetone extraction and precipitation of the rubber from benzene solution gives a product which still contains a small proportion of protein and sugars. Fractional precipitation gives a better product, but it is not entirely free from nitrogen. Purification with methyl alcoholic potash removes all the nitrogen, but the last traces of the alkali are difficult to remove. The diffusion method is then described. This gives an analytically pure rubber hydrocarbon.

In scientific investigations of rubber, many research workers have heretofore given too little attention to the obvious problem of isolating in a pure state the rubber hydrocarbon, or perhaps the several hydrocarbons in the natural raw product. It is timely to gather together and evaluate the various methods useful for this purpose.

I. Acetone Extraction (According to Harries)

The first and for scientific purposes for long the only useful method was that of Harries. It consists of the acetone extraction of rubber, with repeated precipitations from a benzene solution with alcohol or acetone between extractions. This method separates the resins, or, more generally, the oxygen-bearing impurities which are soluble in acetone. The precipitation in itself removes to a certain degree the oxygen-containing substances which remain dissolved in the mother liquors, but it serves primarily to change the surface of the material being extracted. Other substances present which are insoluble in acetone or in the precipitating mixtures are not removed by this method. These consist chiefly of proteins, and, to a lesser degree, of sugars. The analysis of rubber purified by the method of Harries is much closer to the theoretical value than that of raw rubber, but still it does not conform to the theoretical value. Low percentages in the analyses indicate the presence of a considerable quantity of nitrogenous impurities (proteins).

II. Fractional Precipitation

The fractional precipitation described by Pummerer and Koch[2] represents a further advance toward the preparation of pure hydrocarbon. When raw rubber, which has received a preliminary purification according to Harries, is dissolved in benzene and is treated with a mixture of alcohol and benzene to produce incipient turbidity, a "preliminary precipitate" is formed. This contains 30–40 per cent of the rubber mass, with the major portion of the insoluble impurities. The remaining solution ("main solution") furnishes after precipitation a starting material, the purity of which is sufficiently high for many scientific purposes, its analysis corresponding to the theoretical value. Analysis, however, is not a suffi-

[1] For former communications cf. Pummerer and Burkard, *Ber.*, **55**, 3458 (1922); and *Ann.*, **438**, 284 (1924).

[2] *Ann.*, **438**, 295 (1924).

cient criterion of complete purity, since the hexahydrotoluene solution is still turbid, and the nitrogen test is positive.

For the hydrogenation and separation of a crystalline rubber it was deemed necessary to continue the purification until the test for nitrogen was negative, and at the start, until a clear ether solution was obtained. The attempt was made to accomplish this by a systematic application of fractional precipitation. The procedure followed, starting with the "main solution," was as follows:

(1) Treatment of the solution with the precipitating agent until incipient turbidity set in. In this manner the mixture separated in the course of several hours into two layers, a lower, more concentrated solution, and an upper, more dilute.

(2) Precipitation of both solutions by an excess of precipitating agent.

There were obtained from each solution a precipitate and a mother liquor. The precipitates were again treated according to this procedure. By this method two ends were attained. In the first operation the insoluble impurities were concentrated in the lower layer, while the oxygen-containing products remained in the mother liquor after the precipitation. A series of fractionations were carried out, wherein the solvent and precipitating agents, as well as the concentration and temperature, were varied. Benzene, hexahydrotoluene, petroleum-ether, and ether were used as solvents, and acetone or alcohol (usually diluted with the corresponding solvent on account of its milder action) as precipitating agents. Benzene was generally used at the start and petroleum-ether in the later stages of the fractionation. During the fractional precipitation pronounced supersaturation often occurred, most frequently with benzene, so that sometimes by a very small increase of precipitating·agent nearly all of the rubber was thrown down. The quantity of precipitate can best be regulated when petroleum-ether is the solvent and acetone the precipitant. Acetone, on account of its milder action, is a better precipitant than alcohol; a precipitation with acetone accomplishes simultaneously an extraction, since the oxygen-containing impurities are acetone-soluble. The fractionations were carried out with several varieties of crepe and smoked raw rubber. As many as eight fractions were obtained in this manner.

This method, however, was not as completely successful as hoped. Products of increased purity were, however, obtained, which gave a clear solution in hexahydrotoluene, and in part also in ether. But certain removal of the nitrogenous compounds was impracticable, even though in several fractions no nitrogen could be detected. It was not possible, as with substances in true solution, to isolate the impurities present in small quantities by a repetition of the precipitation. On the contrary, nitrogen compounds, probably in colloidal solution, were carried into the last fractions. On account of the variable colloidal properties of the raw material it is a problem to overcome these difficulties. The conditions are equally unfavorable whether broken down rubber, smoked-sheet, or pale crepe or unmilled rubber, such as coagulated raw latex, is employed. But perhaps the methods outlined in this section may be of service in the fractionation of pure rubber.

III. Alkali Purification

In the work of Pummerer and Koch another procedure was combined with fractional precipitation, viz., treatment of the purified main fraction with a methyl alcohol solution of potassium hydroxide, over which the rubber petroleum-ether solution was superimposed, and warmed gently for several days on the steam bath.[3] In this manner the last traces of nitrogenous and acidic substances can be removed, as well as by shaking the rubber solution with a cold methyl alcohol solution of potassium hydroxide. This was tried to prevent decomposition of the rubber as

[3] *Ann.*, **438**, 296 (1924).

much as possible, but the subsequent complete removal of alkali from its petroleum-ether solution or its emulsion, as well as the material lost during the course of the work, makes this procedure useful for only relatively small quantities. Therefore, in conjunction with H. Pahl a method was worked out, the principle of which is related to that above, but the sequence of operations was reversed; the albumin was removed from preserved raw latex by means of an alkali purification in aqueous suspension, followed by fractionation. (See following article.)

IV. Fractional Solution of Raw Rubber

No definite way was found to separate the nitrogenous impurities of a raw rubber solution by means of organic precipitants (II). Fractional solution of raw rubber, on the other hand, accomplishes this result. C. O. Weber claimed to observe two phases when he dissolved rubber.[4] Caspari[5] more accurately investigated the phenomena in various solvents, and proved that in an apparently clear solution, e. g., a benzene solution, some insoluble material is still suspended. Several weeks' settling of this undissolved component in the benzene solution precedes Harries' purification (I), and is very essential according to Harries. Caspari considered the undissolved substance as a rubber-like substance, and concluded on this basis that rubber is not a simple substance. This component is transparent in benzene, and is recognized with difficulty. In petroleum-ether it settles as a definite turbidity. Spence and Stevens questioned Caspari's conception, and were of the opinion that only a slowing of the solubility rate is concerned, and that the difficultly soluble substance gradually goes into solution, leaving only the protein behind.

Three years ago Pummerer and Koch[6] pointed out the necessity of investigating rubber by fractionation in order to determine if it is largely a single substance or a mixture of homologous and associated polyprenes of different constitution. They also found that analytically pure rubber differs greatly in its solubility. Rubber which gives a clear solution in benzene can be purified to give a clear solution in hexahydrotoluene, and by further purification a clear solution in ether. These differences could not always be traced back to impurities containing oxygen, since the analyses were always concordant. For this reason the conception of purification involving the separation of insoluble hydrocarbons from the main mass of the rubber is no longer applicable when they are an essential component of the rubber. Analyses are no longer sufficient for the characterization of a pure rubber.

Feuchter[7] has also recently studied the fractionation of rubber, and has repeated Caspari's investigations. He confirms the fact that a difficultly soluble portion of the rubber remains behind when it is treated with the most varied solvents, especially in the case of ether and petroleum-ether. The main portion, which Feuchter calls "diffused rubber," was isolated by him in about 78–82 per cent yield. He showed that this material possesses the most important properties of rubber. The insoluble residue which contains the entire impurities of rubber, viz., protein, sugar, etc., Feuchter calls the "gel-skeleton," and considers it of little importance. Concerning its chemical nature nothing can be said on account of its impurity. This makes it appear possible that we have here only the foreign substances of rubber, along with some adsorbed rubber.

Using ether or petroleum-ether, according to Feuchter's method, it is possible, with definite precautions, to isolate the so-called "diffused rubber" free from nitro-

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[4] *Ber.*, **33**, 779 (1900).

[5] *J. Soc. Chem. Ind.*, **32**, 1041 (1913).

[6] *Ann.*, **438**, 294, 297 (1924).

[7] *Kolloidchem. Beihefte*, **20**, 434 (1925).

gen, but not, as Feuchter states, with "smoked-sheet." In this case the "gel-skeleton" disintegrates and forms a fine dispersion in the solution, so that decantation is very difficult, and difficulties similar to those occurring in the fractional precipitation occur. Conditions are much better with crepe rubber, and most favorable with coagulated raw latex which has not been milled. Even smoked-sheet and crepe are subjected on the plantations to shorter or longer milling processes, which to a certain extent tear apart the structure of the latex particles, and render more difficult the separation of the insoluble portion from the solid "membranous material" of the latex droplet of Freundlich and Hauser.[8] The best procedure is to dialyze preserved raw latex in order to separate the water-soluble compounds, salts, carbohydrates, etc.; then to coagulate and remove the water and resinous impurities by means of an acetone extraction in a Soxhlet. This rubber, after being dried, minced, and dissolved in ether, gives a solution of "diffused rubber" completely free of nitrogen, which on precipitation with acetone is very easily freed from any oxidation products, and yields analytically pure ether-soluble rubber. In this manner the ether-soluble rubber component can be obtained in a pure form. However, the ether-insoluble portion, of which the rubber-like nature is in dispute, cannot be obtained pure, for it contains all of the impurities of the rubber, particularly the protein, and contains up to one-third of its weight of foreign substances. It was possible by means of the alkali purification of raw latex to make some progress with this insoluble component, which is of prime importance for rubber chemistry on account of the question of aggregation. (See Section III above, and the following communication.)

[8] Zsigmondy-Festschrift, *Kolloid-Z.*, **36**, Erg.-Bd. 15 ff (1925).

The Preparation of Pure Rubber from Latex by Means of Alkali, and Its Separation into Sol-Rubber and Gel-Rubber

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The protein in an ammonia-preserved latex was hydrolyzed with alkali for two days at 50° C. Creaming took place, and the cream was separated, treated twice with alkali, finally washed, dialyzed to remove the remaining alkali, and coagulated with acetic acid. The coagulum was extracted with acetone. The remaining highly purified product, "total rubber," contains an ether-soluble and an ether-insoluble (or difficultly soluble) portion. It is probably a combination of this sol- and gel-rubber that gives rubber its important physical characteristics. The gel-rubber can slowly be transformed into the sol-rubber by means of certain solvents. The hydrochlorides were prepared and the reactions of the pure rubber hydrocarbon with tetranitromethane were studied. The purified rubber can be vulcanized to a soft and a hard rubber, and the latter was found to have exceptionally good electric insulating power.

I. Alkali Purification

INTRODUCTION—Because of the necessity of obtaining the entire rubber content free from impurities with as little loss as possible, and in view of unsuccessful endeavors to separate completely the protein by solvents, the use of alkali[1] was tried. It was evident that this method would remove the protein from a latex suspension of rubber, even if not from commercial raw rubber. The protein is probably adsorbed on the outer shell of the latex particle. Furthermore, the resins, in so far as they are not removed by the alkali, can be separated with acetone. It is interesting that the suppositions were verified—i. e., that in the interior of the latex droplet there is neither protein nor any appreciable quantity of resin. It was reasonable to suppose that by the use of latex in place of technical raw rubber as starting material a fairly uniform and well-defined pure rubber could be hoped for, whereas heretofore one was confined to a raw rubber of varying and difficultly controllable properties. The latex used in the experiments was one to two years old, and was obtained from *Hevea brasiliensis* plantations in Sumatra.

The protein of latex preserved with ammonia is only slowly attacked by cold alkali. Freundlich and Hauser[2] have already tried to separate the protein with trypsin, but not quantitatively. They found a temperature of 37° C. favorable. In the present experiments alkaline hydrolysis was unsuccessful, both at this temperature and at the higher temperature of 45° C. However, when working at 50° C. the disappearance of the protein reaction in the course of several days could be followed. This is rendered possible by the tendency of latex treated with

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[1] An experiment with latex and hot caustic soda has already been tried by A. Koch, and is described in his unpublished Dissertation (Greifswald 1924). Cf. *Z. angew. Chem.*, **39**, 1181 (1926).

[2] Herbert Freundlich and E. A. Hauser, *Kolloid-Z.*, **36**, Zisgmondy-Festschrift, p. 21.

alkali at 50° C. to cream. A hydrocarbon layer rises to the top, and the aqueous alkaline solution, which at first is brown in color and on repetition of the process becomes yellowish in color, settles with the impurities. The hydrocarbon layer is separated and the purification process with caustic soda is repeated several times until the biuret and the ninhydrin reaction disappear simultaneously. The alkali in the cream is then separated by washing, and finally by dialysis. The rubber is coagulated and freed from water and traces of resins by acetone extraction in a warm Soxhlet apparatus. This raw product is the "alkali purified latex"—the pure rubber serving as the starting material for subsequent experiments.

Since it was of particular interest to determine whether the difficultly soluble rubber portions were really rubber or perhaps substances containing oxygen, the entire purification process was conducted in a large round-bottom flask in an atmosphere of nitrogen. The raw material obtained in this manner was already analytically pure, but still contained all of the difficultly soluble rubber portions, the rubber-like nature of which, exclusive of the impurities, is in dispute. Therefore, it is designated later as *"total-rubber"* in contradistinction to the single components. De Vries and Beumée-Nieuwland[3] have carried out similar experiments with fresh latex. According to these experiments fresh latex appears to cream, even when treated with cold alkali.

PROCEDURE—Rubber latex preserved with ammonia, with about 40 per cent hydrocarbon, is treated with an equal weight of 8 per cent caustic soda solution (e. g., 750 grams plus 750 grams) in an atmosphere of nitrogen, and then diluted with distilled water (1250 cc.) so that the alkali content of the suspension is 2 per cent, and is then stirred at 50° C. 8–10 hours per day for two working days, and allowed to stand overnight without stirring at room temperature. During the second night creaming takes place. The lower layer of caustic soda is syphoned off and the cream is treated for another working day according to the same procedure, allowed to cream overnight, then separated and repeated three times more, even though the protein and amino-acid reactions have disappeared meantime. The permanganate reaction of the caustic layer must finally be very faint, so that the green manganate stage persists for several minutes in a very dilute solution. For this purpose, as well as for a good yield, it is desirable to obtain the best possible separation of the suspended hydrocarbon from the alkaline liquor. It is possible to shorten this procedure, especially by a critical examination of the working conditions, but to spare the labile hydrocarbon as much as possible it is inadvisable to use either higher temperatures or stronger alkali. With the procedure described the rubber remains entirely intact.

The major purification was followed by washing out the alkali. The cream obtained as described above was diluted with 2300 cc. of distilled water and was agitated at 50° C. for 8 hours, allowed to cream, and separated. Since creaming often fails when the procedure is repeated, the cream was placed directly in a dialyzer (Gutbier's apparatus manufactured by Mineralchemie A.-G., Oeslau, Coburg), of one liter capacity, and equipped with a very serviceable parchment membrane. To prevent coagulation induced by stirring the cream, the parchment bag was rotated slowly. The dialysis was carried out with distilled water, which was renewed six times, once every three to five hours. With the usual cream of about 20 per cent concentration, the dialysis was carried out until 0.1 cc. of $1/50 \, N$ hydrochloric acid per cc. of dialyzed cream was required for neutralization. If a quantitative separation of the alkali content is desired the cream must be diluted to 10 per cent hydrocarbon. Following the dialysis the rubber was coagulated by

[3] *Chem. Zentr.*, **1925**, II, 2300; *Archief Rubberkultuur Nederland-Indie*, **9**, 694–713, 714–720, Buitenzorg.—The authors studied the behavior of rubber latex toward caustic soda as a preservative and were not interested in analytically pure preparations. Their procedure fails with preserved latex.

the addition of acetone or acetic acid. Acetone does not give a quantitative co-agulation, but for certain purposes, e. g., optical measurements, it was desirable to preclude any possible action of hydrogen ions. Acetic acid coagulation, however, did not show any variations. The rubber was minced for the acetone extraction (warm) in the Soxhlet apparatus. Since the extract contains hardly any resins, the acetone extraction is essentially drying. Therefore, the resins as well as the protein are probably adsorbed preponderantly only on the surface of the latex particles from the serum.[4]

The vacuum-dried rubber, even in thick pieces, was transparent and pale yellow in color, was not tacky and was free of nitrogen. Its ash content, with good samples, was 0.077 per cent.[5] Its capacity for vulcanization was normal. Un-doubtedly this rubber was crystalline in nature.[6] The double bonds were still intact, as shown by a quantitative ultra-violet absorption investigation by Pro-fessor Scheibe in the laboratory at Erlangen.[7,8]

II. Fractionation: Sol- and Gel-Rubber

The purified material described above and designated briefly as *"total-rubber"* still contains all actual hydrocarbon substances of the latex, including the difficultly soluble portions. In colloidal chemical discussions of the rubber system, the dis-persion of a difficultly soluble component in a more soluble fraction plays a large role. The simplest case is where the difficultly soluble portion is a reversible as-sociation product of the easily soluble portion, a two-phase system of a single substance which unfortunately sometimes has been designated as a single phase system. It will be seen later that this simple assumption is inadequate. Aside from protein and other foreign substances, there are at least two phases present in rubber, and the mutual penetration of the two phases plays a major role in the elasticity, viscosity, and crystallization of the rubber. We are indebted to Freund-lich and Hauser for the pioneering microchemical proof that latex droplets consist of a viscid interior and a firm elastic membrane, which when pierced allows the contents to run out. Two rubber phases are evident in this case, provided that the membranous material is actually rubber, and not rubber + resin + protein. Freundlich and Hauser assume that the membranous substance is composed of rubber, without, however, offering analytical proof. In view of this important argu-ment for the two-phase theory, the purification and fractionation of rubber must be regarded as the most important problem in its preparation, a fact which was recognized by the writers four years ago. It is futile in the present state of rubber research to ozonize crude mixtures or otherwise to attempt to explain the structure of rubber by this means. Naturally, we do not wish to detract from the impor-tance of Harries' earlier experiments with ozone in relation to the general structure of rubber. Considering, however, the material balance in the ozonization of rubber, the fate of over 20 per cent of the rubber is uncertain.

In the experiments of Caspari and Spence, and especially in recent ones of Feuch-ter, no proof has been given that the final undissolved residue in the extraction, which according to Feuchter constitutes 18–22 per cent, and which is said to be entirely insoluble in the solvent, is actually the insoluble phase of the rubber hydro-

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[4] Compare the discussion concerning this in "*Kautschuk*," **1926**, p. 90.

[5] Analysis of the alkali purified rubber: samples 0.2035, 0.1634 gram, 0.6559, 0.5276 gram CO_2, 0.2208, 0.1764 gram H_2O. $(C_5H_8)_x$. Theory: C 88.15, H 11.85. Found: C 87.93, 88.09; H 12.14, 12.08.

[6] The authors are indebted to Hauser and Rosbaud for the determinations.

[7] *Ber.*, **60**, 2163 (1927).

[8] The authors wish to extend their sincere appreciation to Alice Loewe for her skilful and tireless help in the preparation of this material in a long series of experiments.

carbon, and is not composed of the usual soluble rubber, which is very firmly adsorbed on the protein and other impurities. This conception closely approaches that of Spence and Feuchter. Feuchter found all the important properties of rubber in his ether-soluble "diffused rubber" and considered the insoluble "gel-skeleton" of no consequence.

SOL- AND GEL-RUBBER—With nitrogen-free *"total-rubber"* it was possible to investigate experimentally the fundamental colloidal chemical question of two phases in rubber. When the ether-soluble portion of minced pure rubber has been extracted, which is termed *"sol-rubber,"*[9] there remains behind a variable quantity, depending on the preliminary treatment, of 20–45 per cent of a difficultly soluble residue in the form of swollen gelatinous pieces, which after drying were proved to be analytically pure rubber $(C_5H_8)_x$, completely free from protein, and containing only a trace of ash (approximately 0.2 per cent). This new rubber component may be termed *"gel-rubber."*

It is certain that the membranous substance of the latex particles of Freundlich and Hauser is isolated in this difficultly soluble portion of the rubber, augmented perhaps by the considerable portion of membranous substance dissolved in the internal fluid. Sol-rubber is pure white and very elastic; gel-rubber before further purification is brown and very tough. The softening temperature of sol-rubber lies between 115° and 130° C.; that of gel-rubber between 145° and 160° C. *"Total-rubber,"* the purified raw material, softens between 130° to 145° C. At the first-mentioned temperature the contours of the individual rubber fibers in the capillary tube begin to disappear, and at the second temperature they are no longer recognizable. A true melting does not take place. The crystallized rubber of Pummerer and Koch became isotropic at 60° to 62° C. and was molten at about 90° C. in a small tube.

The gel-rubber behaves normally when titrated with iodine chloride (according to preliminary tests of Mr. Franzjosef Mann), consuming one mole of iodine for one C_5H_8 group.

As yet it has not been possible to gain any indication that the crystallized, purer, and hence more difficultly soluble, rubber portion is concentrated in the gel-rubber, as might readily be supposed.[10] In the case of sol preparations it is seldom possible to stretch the material to the point (approximately 400 per cent) where interference appears, since the colloidal chemical system, which possesses great elasticity and toughness, has been separated into elastic and tough components. Both preparations after complete cold vulcanization, and even before, provided sufficient stretching is possible, gave interference patterns which were just as strong as those of ordinary raw rubber. Previous tests with hot vulcanization showed that total-rubber vulcanizes considerably faster than the two separated components separately.

Disaggregation of Gel-Rubber

It is known that all raw rubber can be made ether-soluble and tacky by a complete breakdown on the mill, or by "disaggregation" as Harries, and more recently Le-Blanc and Kröger, have called this phenomenon. Only a small quantity of oxygen is taken up during this process.[11] This, however, is not necessary for the reaction,

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[9] This fraction is nothing more than a particularly pure diffused rubber, according to Feuchter, derived from total-rubber. The primary material which has never been milled is more suitable for such an extraction than crepe or smoked rubber. Every milling process tears the membranous substance, and endangers the introduction of these fibers into the sol-rubber.

[10] We take this occasion to thank Drs. Hauser and Rosbaud sincerely for the comparative x-ray investigation of sol- and gel-rubber.

[11] H. L. Fisher and A. E. Gray (*Ind. Eng. Chem.*, **18**, 414 (1926)) found only a small diminution of the iodine number by milling in air. The modification of the Wijs iodine number method for rubber of these authors was used to characterize the fractions.

since it takes place just the same under carbon dioxide. The analytical values for rubber completely broken down in carbon dioxide[12] were the same. Pure rubber (*total-rubber*) can be completely broken down exactly like all raw rubber. It might have been supposed that the phenomenon indicated a solution of gel-rubber in sol-rubber warmed by friction on the mill. However, gel-rubber alone can also be completely broken down, and it then becomes ether-soluble. What takes place here? It is inconceivable that the hydrocarbon chains have been torn apart on the mill. It is obvious that work is being done opposing the supermolecular forces which keep the gel-rubber molecules relatively coördinated and in a condition of aggregation. The molecules interdispersed in this manner cannot resist entry of the solvent and are dissolved. The term "*aggregation*" should only be used in rubber chemistry when an isolated, solvent-free preparation reversibly changes its properties on standing.[13] It is possible that aggregation is the beginning of the net structure, but it may also be a different arrangement belonging in the realm of nuclear development ("Schwarmbildung") (cf. the work of Zocher), possibly a straight linear orientation of the molecules in colloidal chemical shapes.

Gel-rubber can also be rendered ether-soluble by means of solvents.

W. Guendel and A. Andriessen are occupied with the resolution of rubber into still smaller fractions. Here it was seen that a sharp ending of ether solubility, such as Feuchter believes he observed, does not exist, for after ten days' continuous extraction a constant condition is attained where only a very small, but nevertheless weighable, constant quantity goes into the ether each day. This process takes place more quickly with benzene hydrocarbons, the action of which increases from benzene to toluene, xylene and chlorobenzene. Cumene is the best solvent for gel-rubber as well as for other rubbers. The gel-rubber regenerated from these solutions, or from ether, shows a much greater solubility in ether than before. However, it is not identical with sol-rubber, but is probably only a part of the sol-rubber in disaggregated form.

It still remains to be explained how much sol-rubber and how much gel-rubber are present in raw rubber or in *total-rubber*. These problems are difficult because gel-rubber is always carried into solution, and at present it is impossible to determine how strongly the sol-rubber which is present at the start influences the solubility of the gel-rubber during the extraction. Moreover, the gel value naturally depends on the choice of solvent. In the following quantitative experiment in ether, the gel content was 35 per cent. The preliminary treatment of the rubber is of importance in determining the gel yield. In this respect Guendel considers extraction with acetone of utmost importance, which, like every heating, diminishes the gel content, and furthermore paves the way for extraction by swelling of the rubber.

Description of a Fractionation Experiment

All experiments with rubber were carried out under the strictest exclusion of air and light, a carbon dioxide medium being used. During evaporation, only vessels with ground glass joints were used, and temperatures above 40° C. were avoided.

For the separation of *total-rubber* into ether-sol- and ether-gel-rubber, *total-rubber* which had been thoroughly dried in a high vacuum and cut into pieces the size

[12] 0.1326, 0.1512 gram samples: 0.4274, 0.4880 gram, CO_2, 0.1224, 0.1616 gram H_2O. Theory: C 88.15, H 11.85. Found: C 87.93, 88.05; H 12.02, 11.96.

[13] But not synonymous with *association*. If it is desired to reserve the expression "*aggregation*" for an augmented association in solution, reaching colloidal magnitudes, which might not be amiss, then it is necessary to introduce another name, perhaps "aging"* for that which is known in rubber as "*aggregation*." The customary nomenclature should be retained until aggregation has been investigated further. Cf. "*Kautschuk*," **1927**, p. 233.

* [Not to be confused with aging by oxidation.—Translator.]

of barley-corn was treated with anhydrous ether. For the regular experiments these solutions were prepared in 1 per cent concentration. After 0.5 to 1 hour the rubber had swollen greatly and solution lines appeared in the ether when the liquid was carefully rotated for a brief time. This agitation was repeated daily two or three times. The ether-sol-rubber solution (solution α) after three days was decanted in an atmosphere of CO_2 from the gel lying on the bottom into a second agitating flask, and the gel was again treated with about the same volume of ether, corresponding to the solvent removed. This decantation and new addition of ether were repeated four times more; with the solutions β, γ, δ after four days, and with solutions ζ and ϵ, after five days. A determination of solids was made with 2 cc. of the previously weighed solution, and the quantity of dissolved sol-rubber determined. Only the first solution was used for the later experiments, since it contained about 50 per cent of the *total-rubber*. For the isolation of the sol-rubber the solution was placed in a flask with ground glass connections and the ether was distilled off at 40° C. To prevent a diminution of the boiling, a slow, dry stream of carbon dioxide was blown through the liquid. After removal of the ether, the sol-rubber was dried to constant weight in a high vacuum at 30° to 50° C. Constant pressure as determined on the MacLeod manometer is a better criterion than constant weight. The ether-gel-rubber was subjected to the same treatment after it was separated from the last ether solution by decantation. The following table represents a quantitative experiment on the separation of total-rubber into ether-sol-rubber and ether-gel-rubber.

Total-rubber, weighing 4.4128 grams, was treated with 450 grams ether.

| Solution | Solution decanted after ? days | Decanted solution | | | Total rubber dissolved, grams | Total rubber dissolved from original rubber, per cent | Newly added ether, grams |
		Weight, grams	Strength, per cent	Contains rubber, grams			
α	3	351	0.60	2.095	2.095	47.47	350
β	4	326	0.14	0.4458	2.5408	57.58	350
γ	4	318	0.044	0.1388	2.6796	60.72	350
δ	4	369	0.016	0.0599	2.7395	62.08	350
ϵ	5	336	0.016	0.0540	2.7935	63.31	350.
ζ	5	360	0.016	0.0562	2.8497	64.58	...

The gel, freed from ether by evaporation and dried, weighed 1.5596 grams and corresponded to 35.34 per cent of the *total-rubber*.

In the preparation of larger quantities of the sol- and gel-rubber (190 and 135 grams) for vulcanization experiments from 400 grams of *total-rubber*, 2 per cent solutions were prepared in six 5-liter agitating flasks. To obtain a more rapid separation from the gel, the ether solutions, in one process, were filtered through fine-holed filtering plates (without paper), at the same time stirring the gel on the plate with a glass rod, and finally filtering through Swiss silk gauze spread over a second filtering plate. The gel carried through was returned to the gel remaining in the flask by means of a large funnel. In other respects the isolation of sol-rubber and gel-rubber was as before, only on a larger scale.

Combustions of the two rubbers gave the following analyses:

Rubber $(C_5H_8)_x$. Theory: C, 88.15; H, 11.85. Ether-sol-rubber: 0.1320, 0.1456 g. Samples: 0.4258, 0.4382 g. CO_2, 0.1408, 0.1446 g. H_2O. Found: C, 88.00, 87.98; H, 11.94, 11.90.

Ether-gel-rubber: 0.1300, 0.1512 g. Samples: 0.4180, 0.4875 g. CO_2, 0.1392, 0.1612 g. H_2O. Found: C, 87.72, 87.96; H, 11.98, 11.93.

### III. Several Comparative Reactions with our Rubber Preparations

(*a*) PREPARATION OF THE HYDROCHLORIDES OF TOTAL-RUBBER AND ETHER-SOL-RUBBER—Two and one-half-gram portions of *total-rubber* and sol-rubber were separately treated with 250 grams of pure chloroform. After two days the sol-rubber was already completely dissolved to a clear solution. The *total-rubber* was shaken for six hours on the machine, since it still showed flocks of undissolved material (residual gel) after fourteen days. Following this, the solution, even though turbid, was relatively homogeneous. A moderate stream of dry hydrogen chloride was passed through the ice-cooled solutions for four hours. The solutions were allowed to stand stoppered after saturation with hydrogen chloride. The *hydrochlorides* were precipitated with about 80 cc. of absolute alcohol. Tough, white products separated, which became hard and crumbly after twelve hours. The reaction mixture was decanted, and the hydrochlorides were washed three times with ether, filtered and dried $1\frac{1}{2}$ hours in vacuum over concentrated sulfuric acid.

Analyses: $(C_5H_9Cl)_x$. Theory: C, 57.40; H, 8.68; Cl, 33.92. Total-rubber. Found: C, 59.06; H, 8.7; Cl, 31.84. Sol-rubber. Found: C, 59.50, H, 8.75; Cl, 31.48.

F. W. Hinrichsen, H. Quensell, and E. Kindscher[14] have found less chlorine, viz., 30.7 or 30.8 per cent Cl, using ordinary raw rubber, and with the same procedure.

(*b*) THE TETRANITROMETHANE REACTION OF RUBBER—According to Werner[15] and Ostromisslensky[16] tetranitromethane is a reagent for olefin double bonds, since it unites with unsaturated hydrocarbons to give yellow unstable addition products which decompose easily. One of us, in collaboration with A. Koch, has used this reagent in order to prove the completeness of reaction when rubber is hydrogenated. It was found[17] that rubber can react differently from other olefins.

At first a yellow compound is formed, which is visible when solid rubber is introduced into pure tetranitromethane. In hexahydrotoluene solution the reaction mixture at first turns yellow and after five to six days (at 0° C.) turns almost colorless or only faintly yellow or faintly pink, and a stable *addition product* separates slowly, with decolorization of the solution. It does not lose tetranitromethane even when dried in high vacuum for six hours at 60° C. The reagent is bound by primary valences to the rubber. The unsymmetrical constitution of tetranitromethane as a trinitromethanol nitrite has been thoroughly discussed in the works of Harper, Macbeth,[18] Schmidt[19] and Mark.[20] Therefore it may be assumed that an addition product of the formula

$$\begin{array}{ccc} -\text{C} & - & \text{C}- \\ | & & | \\ \text{O:N.O} & & \text{C(NO}_2)_3 \end{array}$$
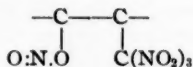
is formed, as in nitrosite formation. It is possible that the nitro groups, through their residual valences, block other double bonds of the rubber, for here, most peculiarly, for the first time not all of the double bonds of rubber enter into reaction with an olefin reagent. One tetranitromethane corresponds to 4.5–6 isoprene groups, when at 0° C. in hexahydrotoluene. All values obtained correspond well to the addition of tetranitromethane, but not to those of nitrous gases.

[14] *Ber.*, **46**, 1283 (1913).

[15] *Ibid.*, **42**, 4325 (1909).

[16] *Ibid.*, **43**, 187 (1910).

[17] Proof of this is found in the dissertation of A. Koch, Greifswald **1924**, unpublished.

[18] *J. Chem. Soc. (London)*, **107**, 87–98.

[19] *Ber.*, **52**, 400 (1919).

[20] *Ibid.*, **59**, 2988 (1926).

When an ordinary type of raw rubber, such as crepe or smoked-sheet, or pure rubber is used, then values of 1:5 are found.

With gel-rubber in suspension, or completely broken down on the mill, the ratio is 1:5. On the other hand, sol-rubber and completely broken down *total-rubber* give the value 1:6. All experiments were carried out in 0.7 per cent hexahydrotoluene solution. Despite the results obtained it is still uncertain that the formation of this addition product makes possible a chemical differentiation between gel- and sol-rubber,[21] since in this reaction colloidal chemical factors as well as the earlier history of the solution appear to have an influence. In several cases where originally more concentrated solutions of pure rubber had been prepared, a *total-rubber tetranitromethane derivative* was obtained which gave the higher addition ratio of tetranitromethane to C_5H_8 groups, viz., 1:4. The tetranitromethane derivative suspended in inert reagents still decolorizes bromine. The yields of tetranitromethane derivative correspond to 90–95 per cent, calculated from the analysis. The results are shown in Table I (cf. Dissertation of H. Pahl, Erlangen **1926,** for details). The following tabulation contains the calculated analytical values for the combination ratios of 1 tetranitromethane to 4 or 5 or 6 isoprene groups:

Addition ratio of tetranitromethane to C_5H_8 groups	1:4	1:5	1:6
Theoretical analytical values % N	11.96	10.45	9.27
Theoretical analytical values % C	53.82	58.18	61.56
Theoretical analytical values % H	6.89	7.52	8.00

Note Regarding Table I Relative to 1, 2, 3—Commercial raw rubber and pure rubber were dissolved in hexahydrotoluene, and after eight days the solutions were decanted from the undissolved precipitate (approximately 5 per cent). *Relative to 4*— The purified cream was not coagulated, but dissolved directly, according to H. Miedel in a 1:1 acetone-hexahydrotoluene mixture. The acetone was subsequently distilled off.[22] *Relative to 6*—The hexahydrotoluene jelly of the ether-gel-rubber dissolved within 42 hours after the addition of tetranitromethane. *Relative to 7, 8*—The breaking down was carried out on a small laboratory mill heated to 50° to 60° C.

The tetranitromethane derivatives prepared at 0° C. were insoluble in all ordinary cold organic solvents. They are non-crystalline, fine powders, according to an x-ray photograph.[23] When gently heated in nitrobenzene or in aniline, an opalescent solution is formed, from which flocks of decomposed material precipitate on heating. At 150° C. the substance starts to turn yellow in a capillary tube, at 175° C. brown, and eventually chars. Since the material detonates on a copper block at 160° to 170° C. it was always mixed with copper oxide for analysis.

The reaction temperature between rubber and tetranitromethane was raised to 75° C. and a large excess of reagent was used, without, however, exceeding the ratio 1:4. Above 75° C. oxides of nitrogen were liberated.

(c) COMPARATIVE VULCANIZATION EXPERIMENTS—*1. Soft Rubber*—It was of interest to know how pure rubber compares with ordinary commercial crepe and smoked-sheet when vulcanized to soft rubber. Hitherto it has been assumed by many that it is not worth while to separate the serum components of the rubber, since they most likely improve the quality of the rubber products, and since the protein acts as an accelerator. The physical properties of sprayed rubber[24]

[21] Repetition of these experiments in cyclohexane solution by Andriessen has given somewhat higher nitrogen values. Here, also, the gel-rubber value is higher than the sol-rubber value, and reaches with precipitated gel the theoretical value of 11.96 per cent N for 1 tetranitromethane : 4 isoprene.

[22] A non-coagulated product of this type was also used for an optical investigation. Cf. *Ber.*, **60,** 2163 (1927).

[23] For this the authors are indebted to Rosbaud.

[24] Obtained by Hopkinson's modification of Kraus' spray process it contains all serum components; *India Rubber J.*, **65,** 267 (1923); English Patent 157,978.

TABLE I

TETRANITROMETHANE DERIVATIVES OF DIFFERENT RUBBERS

No.	Rubber material	Rubber solution used			Amount of tetranitromethane		Ratio of C_5H_8 groups to reaction	Time of reaction, days	Yield, grams	Analyses				
		Cc.	Amt. rubber, gram	By wt. per cent	Grams	Per cent				N, per cent	C, per cent	H, per cent	Ratio of N:O	Ratio to C_5H_8 groups
1	Crepe rubber	100	0.7695	0.99	4	902	1:5	9	1.0916	9.91	58.8	7.51	1:2.12	1:5
2	Smoked-sheet rubber	100	0.6570	0.84	4	1056	1:5	5	0.9612	10.0	58.75	7.7	1:2.06	1:5
3	Alkali purified total-rubber	100	0.7835	1.01	4	885	1:5	2	1.0372	10.01	58.48	7.62	1:2.09	1:5
4	Total-rubber obtained from purified latex with acetone	100	0.668	0.86	4	1038	1:6	6	0.8766	10.4	57.62	7.66	1:2.09	1:5
	Total-rubber obtained from purified latex with hexahydrotoluene													
5	Ether-sol-rubber	100	0.896	1.14	4	929	1:6	4	1.1712	9.01	61.12	8.11	1:2.12	1:6
6	Ether-gel-rubber	100	0.7540	1.00	4	920	1:5	6	1.0492	10.04	58.71	7.66	1:2.04	1:5
7	Purified total-rubber broken down on warm mill for 25 minutes	100	0.7585	0.97	4	1097	1:6	5	0.8124	9.39	61.00	7.9	1:2.01	1:6
8	Ether-gel-rubber broken down on warm mill for 20 minutes	100	0.8148	1.09	4	850	1:5	5	1.0520	9.97	58.08	7.61	1:2.14	1:5

make one cautious in this respect. Experiments with 10 per cent sulfur at 3.5 atmospheres' steam pressure showed that pure rubber behaves very much like the best commercial plantation rubber, both with respect to its rate of vulcanization and its physical properties. The properties of technical soft rubber undoubtedly depend upon the pure hydrocarbon. With 7.5 per cent sulfur, pure rubber requires somewhat longer vulcanization, which is not surprising in the absence of protein as accelerator. The experiments were made with relatively small quantities and are therefore only of preliminary value, as well as those following. (For details see Dissertation of Pahl, loc. cit.)

A comparison of the preparation of soft rubber vulcanizates from pure rubber and from its two separated components, sol- and gel-rubber, showed surprising results. Seven and one-half per cent of sulfur at 3.5 atmospheres' pressure for 210 minutes was employed, which is ordinarily sufficient for complete vulcanization. Nevertheless vulcanization had not proceeded to an optimum cure. With *total-rubber* it had proceeded considerably further (4.24 per cent free sulfur by acetone extraction) than with sol or gel, both of which reacted very little with sulfur (6.56 and 6.96 per cent sulfur soluble in acetone). The experiments must be repeated with more material.

2. Hard Rubber—Pure rubber was converted into hard rubber with 30 per cent sulfur. In this case a favorable dielectric strength was to be expected, since the product contained fewer electrically conducting impurities than raw rubber. In fact, hard rubber prepared from pure rubber had three times the insulating capacity of hard rubber prepared from ordinary crepe. Two comparative samples of pure rubber and crepe were mixed with 30 per cent sulfur, and were heated 240 minutes at 3.5 atmospheres' pressure. The plates obtained were exposed for six months to air before the measurements were made.[25]

A preliminary determination of the test pieces with respect to transverse conductivity by means of galvanometric methods gave practically $\infty\,\Omega$, certainly a value exceeding $10^9\Omega$. The samples were then investigated electrometrically, and the following values for surface conductivity were obtained:

$$\sigma \text{ Pure rubber} = 0.12 \times 10^{-8} \, (1/\Omega)$$
$$\sigma \text{ Crepe} = 0.34 \times 10^{-8} \, (1/\Omega)$$

corresponding to a surface resistance of

$$R_{\text{pure rubber}} = 8.32 \times 10^8\Omega, \ R_{\text{crepe}} = 2.92 \times 10^8\Omega$$

We wish to extend our sincere thanks for the coöperation of the German scientific world, as well as to the Pahl'sche Gummi-und Asbest-Gesellschaft m. b. H., Duesseldorf-Rath, for generously sponsoring our work.
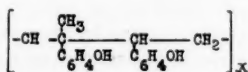
New Derivatives of Rubber

By Giuseppe Bruni and E. Gieger

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(For years, especially from the time of the famous Harries, efforts have been made to synthesize organic derivatives of rubber, both because of their potential value industrially and because they offer about the only hope of solving the great problem of the structure of the rubber molecule. In an unexpected way Bruni has succeeded in preparing certain organic compounds of rubber which open the way to the preparation of numerous other substances which have never been synthesized and which may be of great importance chemically and technically. Bruni and his collaborator, Geiger, have reported the results of their researches so far obtained in ATTI DELLA REALE ACCADEMIA NAZIONALE DEI LINCEI, *6th series, Vol. 5, No. 2, pp. 823-8 (1927), from which this translation has been prepared for* THE RUBBER AGE *by C. C. Davis.—*EDITOR*).*

ALTHOUGH the numerous researches of Harries, Staudinger, Pummerer and their collaborators have in recent years enriched our knowledge of the chemistry of rubber, the number of derivatives of rubber prepared up to the present is very few, and the number of atomic groups or radicals which it has been possible to introduce in the polyisoprene chain is still smaller. The reason for this is that rubber itself and its halides and hydrohalides have only a limited reactivity because of their colloidal nature and their slight solubility.

Among those already known, the most interesting derivative is that obtained many years ago by C. O. Weber[1] by the action of phenol on rubber dibromide. This was considered by Weber to be a phenolic ether, whereas Fisher, Gray and McColm[2] have recently shown that it is a condensation product of hydrorubber and has free phenol groups.

$$\left[-CH - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle C_6H_4OH}{|}}{C}} - \underset{\underset{\displaystyle C_6H_4OH}{|}}{CH} - CH_2- \right]_x$$

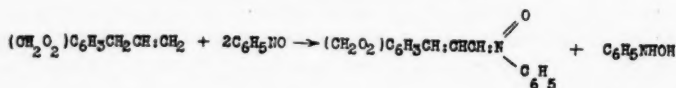[Erratum—The first group in the above formula should read "—CH₂"]

It is in fact soluble in alkalies, and reacts with dimethyl sulfate to give a dimethyl ether. The most significant fact is that up to the present there has been no derivative of the rubber hydrocarbon prepared which contains specific radicals in the actual chain of the

isoprene residue. The only modification of this chain which it has been so far possible to bring about is a transformation into hydro-rubber $(C_5H_{10})x$ by hydrogenation, which was accomplished independently by Staudinger and by Pummerer. This excepts of course the isomerization and cyclization reactions realized by various investigators.

It is obvious that the preparation of derivatives of rubber containing the greatest possible number of atomic groups is of great interest, and above all else *the introduction of ketone, alcohol, amine and other groups in the rubber chain would be of the greatest importance.*

A series of researches has been undertaken which opens the way to accomplish this, and therefore it is opportune to describe the results so far obtained.

In the course of his classic researches on nitrogen compounds, Angeli and his collaborators discovered and explained the behavior of nitrosobenzene toward unsaturated compounds. Thus in 1910 Angeli, Allesandri and Pegnaz, by treating safrole with nitrosobenzene, obtained a compound $C_{16}H_{13}O_3N$ and a considerable quantity of azoxybenzene as by-product. In this way they showed that the reaction proceeds in the following way:

$$(CH_2O_2)C_6H_3CH_2CH:CH_2 \; + \; 2C_6H_5NO \; \longrightarrow \; (CH_2O_2)C_6H_3CH:CHCH:N \overset{\displaystyle O}{\underset{\displaystyle C_6H_5}{}} \; + \; C_6H_5NHOH$$

The phenylhydroxylamine which is formed reacts with a third molecule of nitrosobenzene, giving azoxybenzene. By the subsequent action of phenylhydroxylamine on the yellow compound, there was obtained a mixture of isomeric oximes from which with amyl nitrite was obtained the corresponding dioxymethylenecinnamic aldehyde, thus:

$$(CH_2O_2)C_6H_3CH:CHCH:NOH \; \longrightarrow \; (CH_2O_2)C_6H_3CH:CHCHO,$$
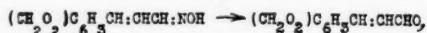
from which with phenylhydroxylamine the original compound is finally recovered.

Even in that publication, the authors recorded the fact that nitrosobenzene reacts with rubber. Five years later Aleseandri[4] resumed the study of this reaction with rubber and obtained an amorphous product which melted 135-140°C and had the approximate composition $C_{58}H_{61}O_9N_5$. He did not, however, succeed in obtaining products of a simpler composition and did not continue the research.

The importance to the chemistry of rubber of these researches of Angeli and his collaborators seems to have escaped later investigators, although a few years ago attention was called to them by one of us (Bruni)[5].

It was therefore believed to be useful to undertake a further study of the reaction of nitrosobenzene and rubber, and to extend this reaction to numerous other nitroso derivatives in order to throw further light on the subject.
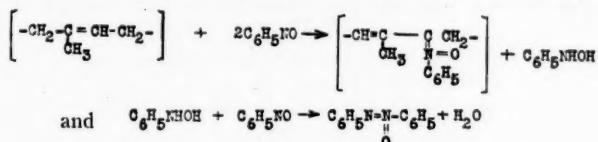
The reaction between nitrosobenzene and rubber takes place readily when they are mixed in benzene solutions in the proportions of 3

molecules of C_6H_5NO to 1 C_5H_8 group, and are then heated for 15 minutes on the water bath. The solution changes from green to a yellowish to a red-brown color. If after cooling, they are poured in petroleum ether, a flocculent substance is obtained which has the composition $C_{11}H_{11}ON$ and decomposes at 135-140°C. By evaporation of the petroleum ether, a large quantity of azoxybenzene is obtained.

Its formation therefore constitutes *a method for the quantitative determination of raw rubber* which is preferable to any so far proposed.

This product still contains a double bond, in fact it readily absorbs two atoms of bromine, giving a *dibromo derivative* of the composition $C_{11}H_{11}ONBr_2$.

This fact in conjunction with the formation of azoxybenzene is a certain proof of the liberation of phenylhydroxylamine, and shows that the reaction proceeds exactly according to the scheme of Angeli:

$$\left[-CH_2-\underset{CH_3}{C}=CH-CH_2-\right] + 2C_6H_5NO \rightarrow \left[-CH=\underset{CH_3}{C}-\underset{\underset{C_6H_5}{\overset{\|}{N=O}}}{C}CH_2-\right] + C_6H_5NHOH$$

and $\quad C_6H_5NHOH + C_6H_5NO \rightarrow C_6H_5N=\underset{O}{\overset{\|}{N}}-C_6H_5 + H_2O$

The product obtained therefore contains the chain of iso-rubber and is a *nitrone of iso-rubber*. It may have the alternate formula:

$$\left[-CH_2-\underset{CH_2}{\overset{\|}{C}}-\underset{\underset{C_6H_5}{\overset{|}{N=O}}}{\overset{\|}{C}}-CH_2-\right]$$
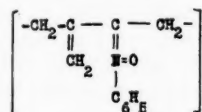
The same reaction occurs when, in place of a benzene solution of rubber, latex of *Hevea brasiliensis* diluted with pyridine is mixed with nitrosobenzene in pyridine. The products by each method have the same chemical composition and differ only slightly in their solubility. *This is the first case where a derivative of rubber has been obtained directly from latex.*

The nitrone is colloidal, and examined by x-rays, it gives photographs which show no indication of even very minute crystals.

The reaction was then extended to homologues of nitrosobenzene, and was found to proceed in the same way. From *o-*, *m-* and *p-*nitrosotoluene were obtained the corresponding *derivatives*.

As was to be expected, nitrosophenols do not react in the manner described, since they are not true nitroso derivatives but behave as quinoneoximes, $O:C_6H_6:NOH$. Conversely the methyl ether of *o*-nitrosophenol, *o*-nitrosoanisole, in which the tautomeric quinone-oxime form is not possible, reacts like nitrosobenzene, giving the *rubber derivatives*

$$\left[-CH=\underset{CH_3}{\overset{|}{C}}-\underset{\underset{C_6H_4OCH_3-o}{\overset{|}{N-O}}}{\overset{\|}{C}}-CH_2-\right]$$
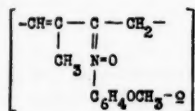
More interesting still is the product obtained by the reaction of ethyl *o*-nitrosobenzoate on rubber, the former of which is obtained by the method of Ciamician and Silber, *viz.*, exposing alcoholic *o*-nitrobenzaldehyde to light.

In this case too, the reaction proceeds as with nitrosobenzene, and from three molecules of the nitroso derivative and one C_5H_8 group there are obtained two molecules of azoxybenzene. From the condensation product there is obtained, by subsequent treatment with sodium ethylate and acidification with hydrochloric acid, a precipitate of the corresponding *acid*:

$$\left[\begin{array}{c} -CH=C-C-CH_2- \\ CH_3 \quad N=O \\ C_6H_4CO_2H - Q \end{array} \right]$$
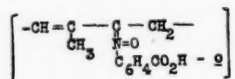
This acid is insoluble in water, and like all the other **derivatives** described, is colloidal. It is, however, readily soluble in aqueous alkalies, and the solutions thus obtained have the character of true salt solutions. It is thus a typical case of a *colloidal electrolyte with a colloidal anion and molecularly dispersed cations.*

$$\left[=C_5H_6:NOC_6H_4CO_2K \right]_x \rightleftharpoons \left[:C_5H_6:NOC_6H_4COO^- \right]_x + x\left[K^+ \right]$$
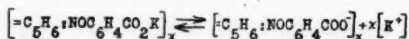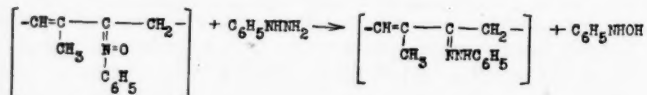
Following this, an investigation was made of the behavior of other nitroso-derivatives, including *p*-nitrosodimethylaniline, *p*-nitrosomonomethylaniline, *p*-nitrosodiphenylamine and *p*-nitroso-*o*-toluidine, which are generally regarded today as possessing a true nitroso structure but which formerly were considered possibly to have quinone structures. The true nitroso nature of *p*-nitrosodimethylaniline was shown twenty years ago by one of us (Bruni)[6] by its isomorphism with *p*-nitrodiethylaniline and by Angelie and Vellardi[7] by its chemical behavior.

These nitroso bases also react easily with rubber, but a description of their behavior is postponed to another paper to be published shortly.

The researches were extended to *gutta percha,* and it was found that it behaved like rubber. The condensation product of gutta percha and nitrosobenzene, *viz.*, the *nitrone of iso-gutta percha,* and its *dibromide* were thus prepared.

Hydroxylamine did not react with the nitroso derivatives and therefore the oximes corresponding to that prepared by Angeli from the safrole derivative could not be prepared.

On the other hand it was possible to prepare the corresponding *hydrazones* by the action of free phenylhydrazine on the condensation product of rubber and nitrosobenzene. The reaction involves the elimination of phenylhydroxylamine:

$$\left[\begin{array}{c} -CH=C-C-CH_2- \\ CH_3 \quad N=O \\ C_6H_5 \end{array} \right] + C_6H_5NHNH_2 \rightarrow \left[\begin{array}{c} -CH=C-C-CH_2- \\ CH_3 \quad NNHC_6H_5 \end{array} \right] + C_6H_5NHOH$$

There is little need of mentioning the importance of the product thus obtained. It is the *phenylhydrazone of a ketone containing the*

carbonyl group in the rubber chain and the name *cauccione* is proposed for this new compound.

The preparation of this new compound opens the way for the preparation of the corresponding free ketone and from this in turn to other derivatives containing characteristic groups in the isoprene chain. By reduction it can also lead to the preparation of aminorubber, which has never yet been obtained. The researches are to be continued in this field.

It also remains to be investigated whether there is any *relation between the reactions described above and the accelerating action of nitroso derivatives.* This subject is also under investigation.

The new derivatives which were prepared include the following hitherto unknown compounds:

Iso-rubber nitrosobenzene
Iso-rubber nitrosobenzene dibromide
Iso-rubber phenylhydrazone
Iso-rubber o-nitrosotoluene
Iso-rubber m-nitrosotoluene
Iso-rubber p-nitrosotoluene
Iso-rubber o-nitrosoanisole
Iso-rubber ethyl o-nitrosobenzoate
Iso-rubber o-nitrosobenzoic acid
Iso-gutta percha nitrosobenzene.

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(2) *J. Am. Chem. Soc.* 48, 1309(1926).
(3) *Rend. accad. Lincei* [5] 19, i, 650(1910).
(4) *Rend. accad. Lincei* [5] 24, i, 62(1915).
(5) *Rend. accad. Lincei* [5] 30, i,(1921).
(6) *Rend. accad. Lincei* [5] 13, i, 572(1904).
(7) *Gazz. chim. ital.* 34, ii, 66(1904).

Importance of Temperature and Humidity Control in Rubber Testing

*Progress Report
of the Physical Testing Committee,
Rubber Division, A.C.S.*

(Dated Dec. 8, 1927)

ABSTRACT

THE purpose of the work which this committee has undertaken is to determine the effect of the variables which influence the results of physical tests on rubber. The investigation has proven that variations in temperature which may occur from day to day in an uncontrolled testing room may affect the physical tests to as great a degree as a 25 to 40 per cent change in the time of cure, while relative humidity affects the results to only a minor degree. Furthermore, variations in the absolute humidity of the room in which the unvulcanized rubber is stored between the time of mixing and the time of curing may affect the tensile strength and modulus of rubber compounds to as great a degree as does the temperature after curing.

It is, therefore, apparent that laboratory tests which are conducted under uncontrolled conditions of temperature and humidity may give highly erroneous results and may even give misinformation which is worse than no information at all. The committee, therefore, recommends that mixed stock prior to curing and cured stock prior to testing be conditioned for not less than twenty-four nor more than twenty-eight hours at 82 deg. F. ± 2 deg. and 45 per cent relative humidity ± 3 per cent and that the testing room be maintained at 82 deg. F. ± 2 deg. If a temperature of 82 deg. F. cannot be maintained for conditioning the mixed stock prior to curing, the committee recommends a relative humidity corresponding to the temperature used which gives an absolute humidity equal to that obtained under the former conditions. The temperature of the testing room should be controlled within the above stated limits, but it is not necessary to control the humidity of the entire room. A small conditioning cabinet in which the standard humidity is maintained has been found to be sufficient.

RECOMMENDATION

The undersigned committee recommends that—

1. Mixed stock prior to curing be conditioned for not less than twenty-four nor more than twenty-eight hours at an absolute humidity of 5.24 grains of water per cubic foot of dry air and cured stock prior to testing be conditioned for not less

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than twenty-four hours at $82°F\pm2°$ and 45% relative humidity $\pm3\%$.

2. The testing room be maintained at $82°F\pm2°$.

3. The time, between removing samples from the conditioning cabinets and curing or testing, be not more than 2 hours.

The temperature of the whole testing room should be controlled closely. It is not necessary, however, to control the humidity of the entire room. Cabinets, located in the room, humidified with the proper saturated salt solution or sulphuric acid solution will produce the recommended conditions.

An agreement has been made with the Committee on Physical Tests of Rubber Products of the A. S. T. M., known as Sub-Committee No. 10 of Committee D-11, whereby the A. C. S. Physical Testing Committee will recommend testing conditions to be accepted as standard by the A. S. T. M. when their use becomes general enough to warrant their adoption.

Your Committee therefore recommends that all laboratories equip to control both temperature and relative humidity as suggested above and report to Sub-Committee No. 10 of the A. S. T. M. to enable them to decide when these test conditions have become sufficiently widely used to warrant their adoption as standard procedure. Though any standard procedure adopted by the A. S. T. M. will apply only to the ageing period between curing and testing, it is recommended that those who are not able to equip to control these two factors should record both temperature and relative humidity during both ageing periods—i. e. between mixing and curing and between curing and testing so that they will later be able to prove to themselves the importance of controlling both temperature and humidity for both periods in connection with all laboratory work, especially for that which is to be published.

GENERAL

The purpose of this Committee is to determine the effect of variables in atmospheric conditions on the physical properties of rubber so that we may know the relative importance of controlling these factors. It is not intended that this work shall include the relative value of specific tests for given purposes or become a research directed towards the development of new tests. It is the specific intent to limit this work to the refinement of tests widely used and considered as routine and standard and not to develop into broader lines of research.

The work has been carried out since the first of the year in conjunction with the Bureau of Standards at Washington by F. E. Rupert as a research associate under the direction of the Committee. The Bureau of Standards has contributed its facilities, and the companies represented by the members of the Committee have defrayed the expenses incurred, contributing $650.00 each. These contributions have carried work thus far and will allow the work to continue until the first of the year. The Rubber Association and the Firestone Tire and Rubber Company (proportion based on rubber consumption) have agreed to support the work of the Committee for 1928 to the extent of $6,000.

It was evident that although considerable work had been done by Stringfield and others on the variations in physical properties of vulcanized rubber caused by variations in temperature and relative humidity during the several stages of preparing and testing samples of rubber, nevertheless the work should be greatly extended. The Committee agreed that a study should be made of the effect of temperature and relative humidity of the air on rubber before milling, during storage before curing, and storing before testing, with respect to the stress-strain, tensile, and abrasive properties of the compounds. It was decided that the stress-strain and tensile properties be studied first pending the development of a more satisfactory abrasion test.

Keeping before us the real purpose of the investigation—the importance of controlling temperature and relative humidity during the preparation of test specimens in a commercial laboratory—the following compounds were chosen for this work. Their suitability for this investigation may be open to criticism and argument. They are, however, representative of type formulae in use today.

TEST FORMULAE

	No. 1	No. 2	No. 3	No. 4	No. 5
Smoked Sheets	100	100	100	100	100
Zinc Oxide	5	5	5	5	5
Sulphur	3	3	3	3.5	3.5
Carbon Black	..	..	..	40	40
Di-ortho-tolyl-guanidine	0.75	0.75	..	1.25	..
Mercapto-benzo-thiazole	..	..	0.5	..	1.0
Stearic Acid	..	..	0.5	..	3.0
Mineral Rubber	..	5.	5.	5.	..
Pine Tar	..	..	..	2.	2.

These formulae represent a laboratory test compound, two gum tire carcass stocks and two high grade tread compounds. With this variety of compounds, we are able to study the effect of temperature and relative humidity upon gum and compounded types, the difference of the effects on two widely different types of accelerators, and the difference in effect produced by varying amounts of common softeners.

Effect of Temperature and Relative Humidity Subsequent to Vulcanization But Prior to Testing

The effect of temperature and relative humidity on cured stocks before testing and during testing was first investigated. Sufficient quantities of compounding ingredients and washed, dried, and blended smoked sheet from three lots were set aside to carry out the investigation of the effect of temperature and relative humidity both before and after curing. A 75-pound batch of each of the stocks was mixed on a 60″ mill and sheeted to gauge and width on a factory calender. After a rest of 24 hours the curing was carried out continuously in two pot presses and was completed within 36 hours, eliminating variation due to ageing in the uncured state.

The Guanidine compounds were cured at 287°F (142°C), while the Mercapto-benzo-thiazole compounds were cured at 258°F (126°C). Each stock was given five cures ranging from an under to an over cure. The five cures of each of the five stocks were conditioned at each of six relative humidities, 0, 20, 40, 60, 80 and 100%, and at each of five temperatures, 5, 15, 25, 35, and 45°C. Thus thirty sets of conditions were studied on each of five cures of

five stocks, making a total of 750 tests. The mixing and curing was done in a factory and the cured slabs were shipped to Washington where the rest of the investigation was carried out at the Bureau of Standards.

The cured slabs were exposed to air at the various relative humidities in conditioning boxes located in a constant temperature testing room.

The temperature of the room in which both the conditioning and the testing were carried out was maintained at each of the five temperatures until all tests at each temperature were completed.

Forty-eight hours was chosen as the period between curing and testing for subjecting the slabs to the test temperature and relative humidity. However, a determination of the rate of absorption of moisture at 100% relative humidity showed that all five stocks absorbed moisture at a fairly rapid rate for six days after which absorption was much lower. Sufficient additional tests with six days exposure were therefore made to determine the effect of this longer period.

Stress-strain curves and tensiles were obtained with the latest autographic Scott testing machine loaned to the Committee by the Henry L. Scott Company and set up in the constant temperature room so that the specimens were tested at the same atmospheric temperature at which they were conditioned.

CONCLUSIONS

While the individual results show undesirable variations which cannot be explained, especially with respect to tensiles, nevertheless a sufficient number of tests were run to make their averages significant of general effects and permit the following generalizations to be made for these compounds:

The effect of temperature is approximately three times as great as the effect of relative humidity changes within the range of each studied in this series of tests. Specimens are highly sensitive to change in temperature, making it absolutely necessary to test them at a uniform temperature and to control the temperature in the testing room within narrow limits. An increase of 18°F is sufficient to cause a decrease in tensile and modulus corresponding to a 25% to 40% decrease in time of cure.

Although the stress-strain and tensile properties of cured rubber are affected by variations in relative humidity, the effect is more gradual and the specimens are not so highly sensitive to relative humidity changes. It will therefore be unnecessary to control the relative humidity in the testing room but will be sufficient to store the cured slabs in a conditioning chamber. A limiting range of ±3% relative humidity is considered necessary for accurate work. An increase of 20 points in relative humidity is equivalent to a decrease in time of cure of 3% to 5%.

Increasing relative humidity and increasing temperature, individually or together, reduces the modulus and tensile of all the stocks.

While there is a slightly increased effect due to continued absorption of moisture for the six days' exposure, the difference in results between two and six days is too small to warrant longer than two

days' conditioning of test pieces. At the higher temperature, the six day exposures gave irregular results, no doubt due to ageing effects.

The physical properties of the gum stocks are affected more than the carbon black stocks by changes in relative humidity.

State of cure has very little influence upon the effect of differences in relative humidity.

The Guanidine and Mercapto-benzo-thiazole stocks showed very little difference in degree of sensitivity to changes in relative humidity.

The softeners exerted only a negligible effect upon the results.

Effect of Temperature and Relative Humidity Subsequent to Mixing But Prior to Vulcanization

The same five compounds were used as in the first part of the work but the range of relative humidities was shortened to 10, 40, 70 and 100% and the number of temperatures investigated was also reduced from five to three, 15, 25 and 35°C, and three periods of vulcanization were used instead of five. These ranges covered the field sufficiently and reduced the amount of work so that the available equipment at the Bureau of Standards could be used and still obtain significant results.

The mixing for this work was done at the Bureau of Standards on a 24″ mill and the stock was sheeted to desired gauge ±.003″ immediately after mixing but at reduced mill speed. Because of the smaller number of temperature and humidity conditions investigated, it was possible to mix all of each stock required in one batch.

The conditioning was carried out in wooden cabinets which were coated inside with paraffin to insure tightness. The doors were also sealed with paraffin. These conditioning cabinets were in a constant temperature room held at 15°C, one being kept at this temperature and the other two maintained at 25 and 35°C respectively by auxiliary heating units in the cabinets. Each cabinet contained four compartments maintained at 10, 40, 70 and 100% relative humidity by sulphuric acid of the proper concentration. Temperature checks in the cabinets were made at top and bottom and held within 1°C. The relative humidity was checked with wet and dry bulb thermometers and maintained within a range of ±3%.

From preliminary experiments it was evident that uncured compounds exposed to 100% relative humidity continued to absorb moisture for some time, so that in addition to a two-day exposure used for most of the work as covering laboratory practice, some tests were run after 12-day exposure, to approximate the maximum effect.

After exposure, all surface moisture was removed and the samples were immediately cured in a four-platen press. Four-cavity aluminum frames were used for molds. The cavities were 6″ square and .070″ thick, giving six test specimens which were broken in every case. The slabs did not vary more than .002″ in thickness from edge to edge. Twelve slabs from three conditioning temperatures and four relative humidities were cured simultaneously.

This method of handling the work eliminated many possible

variables since the slabs for all exposures were obtained from the same batch and all samples for each time of vulcanization were cured at once. The temperatures of platens were tested with mercury thermometers and thermo-couples in the molds and the greatest variation found was 0.3°C. By properly arranging the sequence of operations all cured slabs were allowed to stand for about one month before testing. The test pieces were cut lengthwise of the grain of the sheets.

All vulcanized test specimens were conditioned for two days at 80% relative humidity and 25°C. The testing was done as previously on the latest type Scott testing machine.

CONCLUSIONS

The effect of relative humidity on uncured stocks is very much more marked than the effect of temperature. The importance of these two variables is therefore reversed from their importance in regard to exposure between curing and testing. In the latter case the temperature of the testing room should be controlled accurately while the effect of relative humidity is comparatively small. During the period between mixing and curing, however, the relative humidity should be controlled closely and the effect of temperature is not so important.

The difference in effect between two- and twelve-day exposures is so slight that all further discussion will be based on results obtained after two days' exposures.

The effect of varying relative humidity and temperature between *curing and testing* was in the same direction for all five formulae. The effect of relative humidity between *mixing and curing* is reversed in direction by some of the compounds. Generalizations cannot, therefore, be drawn for this series of tests. It is readily seen, however, that it is of utmost importance to control relative humidity at this point of preparing test specimens and the data indicate that it may be just as important in some cases to examine the effect of a range of relative humidities on a compound as to run a range of cure.

Generally speaking, the undercures are affected more by changes in relative humidity during conditioning before cure than the correct and overcures.

It is also generally true that the effect is more pronounced at the higher temperatures, but this is due chiefly to the great increase in absolute humidity rather than the increase in temperature.

Formulae No. 1 and No. 2, D. O. T. G. accelerated gum stocks with and without Mineral Rubber, show a distinct lowering of the modulus and tensile strength with increased humidity. Formula No. 4, a D. O. T. G. accelerated carbon black tread stock, is only very slightly affected by differences in relative humidity, but what change there is, is in the same direction as for formulae No. 1 and No. 2. Formulae No. 3 and No. 5, both Mercapto-benzo-thiazole accelerated (No. 3 a gum stock and No. 5 a carbon black tread stock), show very marked increases in moduli and some increase in tensile strength with increased relative humidity. In some cases the effect is so great that a change in the per cent figure of the relative

humidity of 20 points is equivalent to ±20% change in time of cure, depending upon the type of stock. In other words, the total discrepancy between a Mercapto-benzo-thiazole gum stock and a D. O. T. G. gum stock might be equivalent to 40% difference in time of cure when the relative humidity changed 20 points. This is adequate reason why different laboratories have not been able to check results at different times during the year, or even from week to week or day to day.

On the other hand, temperature before curing does not exert such a pronounced effect on the test results, although a change of 18°F makes a difference equivalent to a change in time of cure of 15%. This effect is due chiefly to the increase in absolute humidity and not to the change in temperature.

Effect of Time of Exposure and Effect of Delays Between Removal of Uncured Specimens from Conditioning Cabinets and Curing

The differences in effect between two-day and twelve-day exposure before curing and the differences between two-day and six-day exposure before testing were both so slight that it was decided to repeat sufficient of the work to check the possibility of reducing the exposure periods to 24 hours. This was very desirable as most laboratories operate on 24 hour rest periods.

Formulae No. 2, No. 3 and No. 5 were used and the same procedure followed as described in the previous phase of the work.

One group of uncured specimens was conditioned for 24 and 48 hours at 82°F and 55% relative humidity and cured immediately. Samples were tested at 82°F after 48 hours exposure at 82°F and 55% relative humidity. This work was to determine the possibility of reducing the time of conditioning from 48 to 24 hours.

Another group of uncured samples was conditioned for 24 and 48 hours at 82°F and 55% relative humidity and after removal from first conditioning cabinet, duplicates were in each case exposed for ½, 1, 2 and 6 hours at each of the relative humidities 10%, 55% and 100% at 82°F. The samples were then cured. The specimens were tested after 48 hours exposure at 82°F and 55% relative humidity. This work was to determine the effect of delays between removal of uncured compounds from the conditioning cabinet and curing.

Duplicate cured samples were exposed before testing for 24 hours and 48 hours at 82°F and 55% relative humidity to determine the possibility of reducing the time of exposure from 48 to 24 hours.

When this work was started, the Committee had tentatively decided to recommend 55% relative humidity as representing average relative humidity throughout the country.

CONCLUSIONS

There is but slight difference in results between 24 and 48 hour exposure of uncured stock at 82°F and 55% relative humidity. Twenty-four to 28 hours exposure will give accurate results.

Uncured specimens conditioned at 82°F and 55% relative humidity show negligible differences in results when reconditioned for up

to six hours at 10% or 100% relative humidity at 82°F between removal from original conditioning cabinet and curing. Uncured specimens may be allowed to stand exposed to room conditions for periods of time up to two hours before curing for accurate work.

Cured specimens conditioned at 82°F and 55% relative humidity for 24 and 48 hours before testing show negligible differences in tensile and stress-strain properties. Twenty-four hours is sufficient time for conditioning cured test specimens.

DISCUSSION

A report covering the first phase of the work on the effect of atmospheric conditions between curing and testing was read at the Richmond Chemical Society meeting last April and has since been published in the *India Rubber World* (1927) *76,* 139 and *India Rubber Review* (1927) June, 40.

In that report the Committee recommended that the physical testing room be maintained at 25°C (78°F) and that the conditioning cabinets be kept at 80% relative humidity ±5%. Since that time, the members of the Committee have found that 78°F is too low a temperature to maintain in the summer without refrigeration, which, because of expense, should certainly be avoided. 82°F has been found to be a practical temperature which can be maintained ±2° the year around with the possible exception of a very few days in the summer. While this temperature is not as comfortable for workmen as lower temperatures, some laboratories have kept their testing rooms at 85°F and find that the workers soon become accustomed to this temperature.

Eighty per cent relative humidity was recommended at a time when it was thought it might be necessary to condition an entire room and this high humidity was chosen because it is much more economical to raise than to lower the relative humidity of outside air. The present recommendation requires comparatively small cabinets only to be humidified. Forty-five per cent relative humidity at 82°F was chosen because the absolute humidity of 5.24 grains water per cubic foot of dry air is the same as the present A. S. T. M. standard fabric testing conditions of 65% relative humidity at 70°F. This will allow the use of 70°F and 65% relative humidity for conditioning uncured stock and fabric samples if desired. Since temperature alone has a negligible effect on uncured stock, the absolute humidity is specified and any convenient temperature may be used. This allows the uncured stock to be conditioned in a cabinet located in the mixing or curing room and maintained at a constant temperature higher than the room and with relative humidity equivalent to the recommended absolute humidity.

Although sulphuric acid solutions were used to obtain the desired humidities in all the work carried out thus far, the Committee recommends that saturated salt solutions be used because small variations in specific gravity cause considerable differences in the vapor tensions of sulphuric acid solutions.

At present, we have found no data concerning salts or combinations of salts whose saturated solutions will give the absolute humidity (5.24 grains water per cubic foot air) equal to 45% relative

humidity at 82°F in the range of temperatures which will be employed. The following table gives the relative humidity to be used at various temperatures with the available salt solution data. The desired relative humidities are those equivalent to an absolute humidity of 5.24 grains of water per cu. ft. of dry air. The method of calculation described by Spencer (Int. Crit. Tables, Vol. I, p. 67) is used. The percent humidity is arrived at by dividing the aqueous tension (P_1) of the saturated salt solution by the vapor pressure (P_2) of pure water at the same temperature. Data for P_2 are from Landolt-Börnstein, Ed. 5, p. 1317.

Desired		Data for Nearest Salt					Source
Temp. °F	R.H. %	Salt	Temp. °F	R.H.= P_1/P_2 %	P_1 mm.	P_2 mm.	
60	90.5	Rochelle salt*	60	87.9	11.6	13.2	Lowry & Morgan, J.A.C.S.
60	90.5	Na tartrate	60	91.6	12.1	13.2	46, 2192 ff.
65	76.5	Na Cl	65	77.0	12.14	15.77	Speranski, Z. Phys. Chem. 70, 526.
70	65.0	NH$_4$NO$_3$	70	63.2	11.86	18.76	Edgar & Swan, J.A.C.S. 44, 570.
70	65.0	CoCl$_2$—6H$_2$O	70	68.2	12.8	18.76	Derby & Ingve, J.A.C.S. 38, 1439.
75	56.0	Mg(NO$_3$)$_2$6H$_2$O	76	52	..	..	Obermiller, Z. Phys. Chem. 109, 145.
75	56.0	NaBr—2H$_2$O	68	58	..	..	
80	48.0	Ca(NO$_3$)$_2$—4H$_2$O	80	49	..	..	do
82	45.0	do	82	48	..	..	do
85	41.0	NH$_4$NO$_3$	85	42	13.0	30.75	Landolt Börnstein
90	35.0	MgCl$_2$ 6H$_2$O	90	33.5	12.1	36.07	do

*Which has not been heated above 104°F.

It is plain that more salts or combinations of salts whose saturated solutions will give the desired relative humidities at the higher temperatures will have to be found before saturated salt solutions can be used. Until proper salt solutions are found, sulphuric acid solutions of proper concentrations can be used if adequate specific gravity control is maintained. Wet and dry bulb readings should be taken when determining the proper concentration of acid since the size of the conditioning cabinet may have an effect.

Data on sulphuric acid solutions for humidity control are found in an article by R. E. Wilson in *J. I. E. C. 13, 326* (1921) under heading of "Humidity Control by Means of Sulphuric Acid Solutions with Critical Compilation of Vapor Pressure Data."

Water absorption data show that both uncured and cured stocks continue to absorb moisture for several days but all of the work thus far shows negligible differences in tensile and stress-strain properties after 24 hours conditioning. The first two phases of the present problem were carried out with 48 hour and longer conditioning periods, but the later work showed substantially no difference between 24 and 48 hour conditioning periods, hence the recommendation to condition for not less than 24 hours.

FUTURE WORK

Sufficient tests will now be made to determine the importance of effect of changes in relative humidity and temperature before milling.

For the next major problem the Committee has decided to investigate the effect of relative humidity and temperature on resistance to abrasion when stocks are exposed both between mixing and curing and between curing and testing. This work will not be

concerned with the correlation of abrasion tests and service but will be carried out on two different types of machines where tests are readily duplicable.

THE COMMITTEE

E. R. BRIDGWATER	E. I. Du Pont de Nemours & Co.
D. F. CRANOR	Binney & Smith Co.
E. B. CURTIS	The United States Rubber Co.
J. W. SCHADE	The B. F. Goodrich Co.
N. A. SHEPARD	The Firestone Tire & Rubber Co.
A. A. SOMERVILLE	R. T. Vanderbilt Co.
W. W. VOGT	The Goodyear Tire & Rubber Co.
P. L. WORMELEY	Bureau of Standards
J. E. PARTENHEIMER	The Fisk Rubber Co., *Chairman*